VOLUME 16, No. 11 NOVEMBER, 1937

REFINER
AND NATURAL GASOLINE MANUFACTURER

A GULF PUBLISHING COMPANY PUBLICATION

The Look Box

THE Refining Division of the American Petroleum Institute at the annual meeting in Chicago this month, held three technical sessions at which problems of varying nature, but all of importance, were studied. Following custom established several years ago by THE REFINER, all of the important technical discussions presented before these meetings are published in this issue. Among these papers is the review of a decade of cooperative research on the chemical constitution of petroleum conducted by the American Petroleum Institute and the National Bureau of Standards, as presented by Dr. Frederick D. Rossini. Dr. R. T. Goodwin, Shell Union Oil Corporation, discussed fuel oil production and use, with emphasis upon future outlook for supply in the United States. The influence of fuel characteristics upon high-speed Diesel engine performance was considered by G. A. Hope and W. S. Mount of Socony-Vacuum Oil Company, Inc.

A. P. I.

The manufacture of motor fuels by the polymerization process was discussed in a paper prepared by Gustav Egloff, J. C. Morrell and F. F. Nelson of Universal Oil Products Company. E. H. McAllister, Shell Development Company, discussed the catalytic polymerization of butylenes by sulfuric acid. S. D. Heron, of Ethyl Gasoline Corporation, presented a paper on experience with aircraft operation on the new fuels of 100 and higher octane number. Developments in the field of motor fuels were reviewed at the sessions. T. W. Legatski and R. R. Couch of Phillips Petroleum Company discussed the fuel systems of 1937 motor vehicles. The effect of altitude on anti-knock requirements of motor fuel was discussed by Neil MacCoull, K. L. Hollister, and R. C. Crone of The Texas Company. Reports of road and laboratory knock tests were discussed. The group of papers presents an up-to-date correlation of technical and engineering data on several of the more important problems confronting the petroleum refining industry.

PRELIMINARY investigations indicate that the petroleum refining industry in 1938 is going to continue the marked activity in refinery and natural gasoline plant improvement and construction which has been witnessed during this year. It appears now that construction work, both in reconditioning and improvement and in entirely new construction during next year may be about equally divided between the United States and foreign countries. World capacity totals about 6,000,000 barrels a day with around 4,000,000 barrels capacity reported in this country. The 2,000,000 barrels of foreign capacity, widely distributed through some 32 countries, is not sufficient to meet growing foreign needs. The foreign work will be done in practically all countries where refining industries exist, such as Europe, South America, the Orient, East and West Indies, Russia, with some work in Asia. There is likelihood of another South

Construction

American country establishing a refining industry within its boundaries provided exploratory work discovers adequate crude supplies next year. Both the foreign work and domestic work at present is primarily concerned with modernization of cracking facilities chiefly through the installation of combination and selective cracking units, some reforming, further use of polymerization and hydrogenation, and additional solvent dewaxing and solvent extraction systems.

Refineries in this country have been steadily improving processing facilities. A dozen or more large improvement and expansion programs are under way. Further it is known that virtually all of the major refining concerns have plans for further modernization and improvement during 1938, although the actual carrying out of these important plans hinge to a large extent upon the presently disturbing political-economic situation. When the industry's leaders can begin to see through the maze of conflicting variables now presented by the general economic scene and determine to some extent at least that progress will be made toward better times, then those plans now on the boards will begin to go into actual construction stage.

Estimates coming from various industries at the moment, especially the automotive industry point to continued improvement in the general situation next year. Economists within the petroleum industry who last year forecasted a 7½ percent increase in gasoline demand for 1937, only to see that increase reach 10 percent above last year, are now predicting an increase in demand for 1938 of 5 to 7 percent for 1938. If the several industries now studying conditions for 1938 are right, the petroleum refining industry will do well to get its processing equipment in good shape to take care of the better business indicated for next year.

Ickes Warns

AFTER 1066 days Harold L. Ickes, Secretary of the Interior came back to Texas to admit an error and leave warning. As the speaker before the annual banquet of the Independent Petroleum Association of America, October 15, he said that state regulation had come to better results than anticipated.

The time element of 1066 days was his own play on words to draw a contrast between his speech before the American Petroleum Institute at Dallas and his appearance in Houston. In Dallas he made remarks, which he said, "probably wounded the audience as much as it did the speaker."

Friday night in Houston he said, "I am glad to say that I am with a much lighter heart than that which I carried on that other occasion. The burden of responsibility, to a large measure, has been shifted to other shoulders than mine. It now rests primarily with the state authorities and with the oil industry and I say candidly and with great cheerfulness that they have carried on the job better than could have been anticipated."

He paid tribute to the industry for its part in economic recovery, its current field activity and its record output, which were the basis of his warning.

"The continuous and ever-mounting demand for petroleum products only emphasizes, in my mind, the need for an increasing interest in conservation and the desirability of a serious study of the adequacy of the oil reserves of the nation," was his warning.

He designated conservation as "the efficient development and prudent use of our natural resources without waste or needless destruction."

After recounting the many avenues through which oil enters into functioning of civilization, he offered the following as a recommendation of policy for the nation and for the industry:

"We use in this country, principally from our own supply, about two thirds of the oil consumed in the world. Simple arithmetic applied to this formula will reveal that we in the United States are using up our oil reserves at a faster rate than the rest of the world. Unless this trend is checked we will be faced with an oil shortage here in advance of a corresponding shortage abroad."

He classed the Interstate Oil Compact Commission, the Connally act and state conservation authorities as doing generally favorable work in seeking a balance between supply and demand for oil. But the chief responsibility for a stabilized industry was checked back to the industry itself with these closing words:

"You can not expect legislatures to enact adequate laws, regulatory commissions to issue suitable orders, courts to render proper decisions or the public to support what you are doing unless you agree on the fundamental principles which govern the efficient and wise use of oil. In addition to continuous research, there is need for a dissemination of knowledge by which the industry will train itself and prepare the way for an adequate understanding among those who regulate its affairs and by those who consume its products.

"Standing firmly upon its own feet and with the principles clearly established and announced a program of oil conservation, which is that and nothing else, is certain to win the support of a fair-minded public and its representatives in the halls of legislation. I urge that you proceed promptly to this task as we cannot await the day of scarcity before correcting methods that cry out for correction.

"The responsibility for the future of oil in our nation rests mainly in the hands of the oil industry. With this responsibility will go credit for accomplishment or blame for neglect of the opportunity."

Dr. Howe was a guest speaker at the General Session November 11, 1937, of the Eighteenth Annual Meeting of the American Petroleum Institute, Chicago

Significance of Petroleum Research

Its Interest to the Public, Its Necessity to the Industry

H. E. HOWE

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AT the outset it should be emphasized that the observations in this discussion are those of one in no way connected with the petroleum industry. The viewpoint is essentially that of a layman sympathetic with research and highly appreciative of the results it has produced. Included among them are not only those which contribute directly to the security, enjoyment, and prolonging of life but, as well, those research projects the results of which may have no immediate industrial application, but which are valued because they add to our store of knowledge and hence are potentially of vast importance.

In thinking of the petroleum industry, it is practically impossible to separate it from the automotive industry; for, while petroleum was discovered and utilized some decades before the advent of the automobile, it is the requirements of that modern contraption that have influenced the development of the industry and, until very recently, became almost the sole factor in determining the trend of its research. Indeed, as Dean F. C. Whitmore has said: The time may come when we shall deprecate the way in which the automotive industry shunted petroleum research into a channel which has for so long blinded many to the possibilities of crude oil as an invaluable source of raw material for unnumbered products.

We are impressed by the fact that these great industries, petroleum and the automobile, have had their development and enormous expansion since we entered preparatory school. It seems incredible that there were only four motor vehicles in the United States in 1895; 16, the following year; and still but 90 in 1897. We remember distinctly running to the front gate to see, to us, the first automobile chug by at the amazing speed of 15 miles an hour. Even so, it was not until 1904 that we had our first real automobile ride—although by that time, including trucks, of which there were 410, we had accumulated in the United States 55,000 motor vehicles. That was 1904; in 1936 motor-vehicle registrations had reached 28,221,291.

Unquestionably, the average man who buys a car or other motor vehicle, or who installs an oil burner, never stops to wonder whether there will be fuel and lubricants to operate the motor and to heat his premises during the service life of the equipment. To us that is one evidence of the reliance which the public has come to place upon the petroleum industry, although we must remember how casually we moderns accept what is laid at our feet for our use, and how much we take for granted.

Sir William Bragg, the eminent British physicist, emphasized this in the following way:

"It is easy and fascinating to suppose that a new invention is found as complete and clean as a nugget of gold, as unexpected, and as unconnected with its surroundings, and finally as readily convertible into cash. The truth is very different. Science does not increase by constant addition of new facts to old, as a library increases by the addition of new books, or a museum by the addition of new specimens and curios. Science grows like a tree which shoots out new branches continually and at the same time strengthens the old, always growing higher into the light. Like the tree, science needs wise cultivation. The nourishment of the tree and its training and pruning have their true counterparts in science. In both, the fruits come as the reward of skill and labor.

"The fruits of science are first seen when they are brought to market, and it is vaguely supposed they were picked up somewhere and somehow in the condition in which they appear. Perhaps they were made by the man who carries the basket. It is not realized that the fruit comes at the end of a long process, and that even a little application of science may be the result of unseen labor and growth for many years. It is not so easy to develop scientific results as to grow an orchard; the growth of science is not so much under our control as the growth of nature."

And so during the lifetime of many of us the petroleum industry has been required to find ways, beginning with no market for the gasoline, to produce for domestic consumption in 1936 over 18,000,000,000 gallons, with a total consumption for the year of 20,226,822,000 gallons, and a domestic consumption of lubricating oil in the same year of 724,638,000 gallons. This supply is for all internal combustion motors, whether on the highways, in the air, or in the sea, as well as stationary equipment; but it does not include Diesel fuel—and, of course, omits fuel oil. In the brief period under discussion we have seen an industry change from the time when a little gasoline might sometimes be worked off in the kerosene, just to get rid of it, to the days during the War and before the full development of cracking when the motorist complained with some justice that kerosene was being worked off with gasoline.

CHANGE AFTER CHANGE

There are many other changes. We recall that with the first car we bought came instructions to have carbon removed every 5000 miles, to buy a quart of lu-

bricating oil every time we bought 5 gallons of gasoline, and to change the oil every 500 miles. We bought cup grease and, according to directions, laboriously turned up a considerable number of grease cups at each designated mileage interval. Those were the days when all except rabid enthusiasts put up their cars for the winter, because starting the car in cold weather was quite a proposition and, if it did start, the motor was allowed to idle for several minutes for safety's sake to be sure that the oil and other lubricants had become sufficiently warm to insure some protection against excessive friction of metal against metal.

Many of these things, indeed all of them, have changed for the better, and we may say that the difficulty frequently arose through a lack of cooperation between those who designed the motors and other equipment and those who produced the fuels and lubricants. The improvements for which we are most grateful have come about through wholehearted and close cooperation between these scientists from two industries, particularly during the last 15 years. Much that can be said in praise of modern motor performance is a tribute to the research underlying present-day motor design and construction, quite as much as to improvement in fuels and lubricants.

But how has this enormous burden of a twentyfold increase in gasoline demand in only 25 years been carried so well by the industry? It has only been possible through the application of research; the development of new ideas; the application of science and engineering; the contributions of closely related, and even remote, industries; and not a little of what the late Dr. Teeple described as "patient, educated money."

INDUSTRIAL ACCOMPLISHMENTS

High in the inventory must be placed the brilliant research leading to the deevlopment of geophysical methods for the discovery of crude oil. Geophysics arrived in the petroleum industry at a time when other discovery methods were lagging. The refraction seismograph was first used in the United States about 1923, and the reflection seismograph in 1926. The rate of discovery has been very greatly augmented by the use of these new methods and their many refinements, and it is estimated that American petroleum companies spent approximately $35,000,000 for geophysical exploration during 1936, but the results have been of the greatest importance to the public because of the uncovering of oil reserves which could not have been found in any other manner; savings to the industry in greatly decreasing the number of dry holes, each one of which has cost from $50,000 to $150,000, thus saddling normal business expense with a colossal waste; and because it has produced a definite tendency to keep the price of petroleum products at a lower level. With the consumption of petroleum products at an all-time high, it is obvious that, unless the discovery of oil can keep pace with consumption, prices must inevitably rise.

To the layman, and no doubt to others, the ability of these scientific methods to produce data which can be interpreted to indicate conditions from 500 feet to 30,000 feet below the surface is indeed miraculous. The cost of securing such data, not only as it applies to great depths, but even to the coverage of enormous areas, by earlier procedures would quite obviously be prohibitive. Even the geophysical method is being improved; and the present technique, which consists in sometimes connecting a number of electrical seismographs arranged in a row in series and using as many as 12 instruments in a group, makes it possible to secure records in areas heretofore unworkable, and has been important in permitting work over expanses of territory that are indeed vast. According to recent statements, oil exploration still involves large financial risk, and Dr. Frederick Lahee states that even in 1936 the ratio was 6.83 feet of dry hole drilled for each foot of new producing wells for wildcat drilling in the southern states. It would be a salutary thing if the public could realize not only the importance of this work, as such, but appreciate it as one bit of evidence that petroleum operations are not all profit.

OIL WELLS GO DEEPER

Then the question of deep drilling. How widely does the public know what is involved in going down 12,786 feet, as has been done in Texas? The first oil well was drilled laboriously during a number of months to the depth of 69½ feet. Quite different is it to drill down two miles—with what that requires in the strength of a derrick, crown block, and traveling block which holds the weight of this twisting pipe suspended in the hole, and the expense involved in the periodic work of hauling it up, section by section, to change the bit or add new lengths of casing—to say nothing of being prepared on an instant's notice to combat 2000 or 3000 pounds of gas or oil pressure and avoid the wild wells which used to be so common in deep drilling. The multifarious contributions of science which have made possible drilling such a hole, or even a much shallower one, in a straight line comprise a fascinating story; and a conception of the dimensions involved and the factors influencing success makes one wonder that the drill ever hits the target.

The development of the technique for the flooding of old and depleted oil fields, to yield larger amounts of crude oil, is another contribution of research; and the maintenance of gas pressure in oil fields is a part of the same technique. Chemical methods have not been lacking for increasing the flow of oil, and in late years acidation has played an important part where limestone oil reservoirs occur.

One might devote unlimited time to the discussion not only of what has been done, but what remains to be done, in promoting the discovery of oil reserves and drilling unerringly to them—and there is perhaps no more important phase of petroleum research, whether viewed from the standpoint of the industry or the public. Obviously, we can do no work on petroleum without maintaining an adequate flow of crude oil. No wonder then that the industry continues its research program on the fundamentals pertaining to the origin and discovery of petroleum. The industry waits constantly for the results of such research, and no urgence is required to see that they are immediately applied.

Even with an increasing supply of petroleum, without research upon it, it would have been impossible to provide suitable motor fuels in the quantities now demanded and concurrently maintain a reasonable price. We shall have something to say later about the petroleum industry as a tax-gathering agency. Exclusive of taxes, the retail tank-wagon price of gasoline, which was $0.21 a gallon in a certain month in 1926, was only $0.142 per gallon in the same month of 1936, and $0.144 in the same month of 1937; and meanwhile it has been necessary to produce a greatly-improved fuel. When we seriously consider the importance from every point of view, including social implications, of that great trinity —light, heat, and power—and realize how inseparable is the petroleum industry from it, we may gain a new appreciation of research and its application by the industry. It is indeed an achievement to increase the volume of better products and to lower prices, notwith-

standing the variable factors which have entered into the cost of production, maintenance, and distribution.

PROGRESS IN REFINING

This brings us at once to a major contribution in the processing of petroleum, viz., the cracking process. It will be recalled that, when cracking first made its bow, the gasoline made by the process was regarded as inferior. The steady development of cracking has not only contributed enormously to the improvement in gasolines—producing those with high octane number and other desirable characteristics—but now straight-run gasoline is reformed to make it equal in quality to the cracked variety. Indeed, progress has been so rapid that great installations, costing millions of dollars, have been erected with a full knowledge that, at the current rate of progress, they may be partly—if not wholly—obsolete in 5 and, at most, 10 years. It's an industry that requires a lot of courage. Our supply of high-grade motor fuel has been enormously increased by the development of these methods; and we are told by one authority that, had it been necessary to have produced the amount of gasoline used in 1936 by the methods employed before cracking had been developed, the world would have consumed not less than 1,865,000,000 barrels more crude oil in 1936 than it actually did consume. The figures themselves are sufficient emphasis of what this research, through the conservation of a natural resource, has meant to the public. And, mind you, concurrently there has been a steady improvement in the quality of the gasoline made.

Let us see those figures again that they may not be forgotten: It would have required 3,607,000,000 barrels of crude, in place of 1,742,000,000 barrels, in 1936 alone to have produced throughout the world the same amount of gasoline by straight distillation of the crude—without cracking. Then it would have been necessary to locate more oil fields, expand storage, and increase refining capacity. Prices would have advanced. This type of service in the public interest is not reflected adequately in mere terms of monetary considerations.

Another way to conserve a resource is to devise means for accomplishing more with a unit quantity than previously has been possible. We have no way of estimating how many more millions of barrels of oil have been saved, thanks to the better quality of gasoline produced which, in turn, has made possible more efficient motors, with the result of more miles per gallon per car. Engines have been made smaller and lighter for a given horsepower rating. This has resulted in a decrease in the load to be carried by the vehicle. At the same time the modern motor gives better power and performance without increased fuel consumption; indeed, it uses less than its predecessors. Let it be said again that only part of the gains indicated are due to the improved fuels, for much of it must be credited to changes in engine factors such as speed and volumetric efficiency; but the two groups of improvements have been the result of cooperative effort.

More recently a notable development—polymerization—has made possible—although it is not fully realized as yet—the production of from 10 to 20 percent more gasoline than is now being produced, and this without increasing the rate of crude withdrawal from underground reserves. By the catalytic polymerization of *iso*butylene with subsequent hydrogenation, the industry is today producing a large quantity of *iso*octane—making possible a supply of 100-octane gasoline to commercial and army airplanes for a class of service impossible with ordinary aviation gasoline. At the Second World Petroleum Congress this year, *iso*propylether—another product of research—was urged as a new blending agent for aviation fuel of 100 octane number. It is estimated that in 1936 the supply of raw materials was sufficient to have made 850,000,000 gallons of such gasoline. By a different process of polymerization, it is possible to produce aromatic hydrocarbons should they be needed for dyes, explosives, or for other purposes.

The recovery of casinghead, or natural, gasoline has been an important contribution; for it has added millions of gallons to our supply of high-grade motor fuel, and has come with the development of efficient and economical means for recovering and stabilizing this light gasoline. But more than that, there is an important, though less recognized, natural gasoline industry within the refineries themselves, where the conservation of light ends produced in cracking and distillation has further and materially increased the supply of motor fuel.

FURTHER DEVELOPMENT

Under this same heading of maintaining, and indeed increasing, the supply of fuels without proportionate demand upon crude oil should be placed the notable work on hydrogenation development in this country. This type of research is most difficult and expensive; and, while it has its immediate application, there is good reason to believe that its greatest service to the public will be in the future. We look upon it as one of the important methods to be applied where the petroleum molecule is to be taken apart and then re-assembled to produce a fuel, an illuminant; or a lubricant in accordance with exacting specifications. Further, it is one of the factors—along with cracking, distillation, and polymerization, to name but three procedures—which, when economics or necessity make it desirable, will enable petroleum technologists to convert crude oil entirely into internal-combustion motor fuels. The costs of today may not need to advance very much to justify such procedure. In the future it may be needed to produce motor fuels from coal and like materials.

In all this work we must not lose sight of notable and essential contributions from other fields. Not infrequently research and its application to petroleum technology have been obliged to wait on improvements in metallurgy—the design and construction of huge conversion and catalyst chambers to stand high temperatures and pressures; the perfection of the modern tube still and fractionating tower, to replace the old shell still equipped with air condensers; the important contributions of those long experienced in design, erection, and operation of distillation equipment, heat exchangers, control and recording devices, and the multitude of items which make up the impressive equipment of the modern oil refinery—all have a part in this modern program. The development of treating processes using fuller's earth as the contact catalyst has served to increase the yield and quality of cracked gasoline, as well as lubricating oils, without contributing to the cost of production.

While the improvement in octane number has been brought about to a considerable extent by cracking and polymerization, one of the chief contributions to this important result has been the conception of what actually causes knocking in an engine, and the subsequent research to find a remedy. This led to the use of additional organic compounds of lead—notably tetraethyl lead. With perhaps 80 percent of all the gasoline sold through American filling stations today containing tetraethyl lead, it is not necessary to go into detail relative to the discovery, development, and use of this reagent. We recall that in those early days, when gasoline containing this compound was temporarily off

the market while changes were being made in the method of distribution, etc., we were driving with a friend in his rather ancient car which was having some difficulty, especially on the hills. I can still recall his cry of joy when, coming into one hamlet, he saw a sign "Ethel is back." Joyfully he made his purchase, and benefited from the immediate improvement in the performance of the old machine. Our public perhaps does not realize just what it has meant to it to be able to use this and other high anti-knock fuels, and should be told that it has brought an increase in power with a great decrease in both the size and the weight of the engine—with resulting economy to the automobile user that should be obvious without further and labored elaboration. Incidentally, it has brought a new industry into being, and has caused another to expand.

The processes for stripping hydrogen sulfide from refinery gases and natural gases have been developed to a point of high efficiency and economy. They permit the recovery of the gas which may be utilized as a fuel where the quantity of sulfur is too small to be valuable, or as a source of elemental sulfur where economy dictates that procedure. The net result is a process which purifies the gas (a particularly important procedure where polymerization is concerned) and at the same time supplies by-products frequently of definite value.

Another notable contribution of science to the industry, of direct benefit to the public, has been the development on a large scale of methods for stabilizing gasoline by removing small amounts of hydrocarbons of very low boiling point, and thus reducing vapor lock—the cause of much profanity. This contribution has made possible the development of gasolines which will give dependable service in winter weather; and this, like many other fuel improvements, has made its contribution to the advances in the design of the gasoline engine. In this same class perhaps should be placed the discovery of those chemical inhibitors against the oxidation of gasoline in storage that free us from the evils of gum formation; and the development of seasonal products by the industry, such as gasolines designed to give the best results for summer in those sections of the country where the variations in the weather are great enough to give a change which is notable.

The production of fuels for aviation and for Diesel engines have presented their own problems, and have received their full attention. We have mentioned the importance of *iso*octane production to aviation, which still is of prime interest to a relatively small proportion of the public; and we have not yet become much acquainted with the Diesel engine in the United States, although its performance in streamline trains, in manufacturing plants, and in many other types of service, has been the subject of much discussion and publicity. Diesel-powered trucks and buses are within our purview; and the research on the characteristics of such engine fuels promises to make available ultimately quantities of oil fuels suitable for high-speed automotive Diesels, giving them some advantages over gasoline engines for certain types of service, such as long-range trucking.

It may be interesting to recall that 500,000 motor boats now ply waters of the United States—some on business, and many on pleasure bent—but requiring a continuous supply of motor fuels and lubricants. Fuel for racing motor boats has become a high-speed specialty. The farmer has come to depend to a great extent on the products of petroleum to help him attain the more abundant life of which we hear so much over the radio. As long ago as 1930 there were 5,000,000 motor cars and trucks on the farms, and in 1936 there were 1,248,337 tractors. In those states where the uncertainties of weather at times play havoc with a perishable crop, oil fuels in orchard heaters are used to fight the frost. It may be noted that in California, Oregon, and Washington alone, in the season of 1936-37, it required 1,742,500 barrels of orchard heater oil to operate these defenses.

We in the United tSates, in 1936, consumed 405,000,000 barrels of oil for producing heat and power. When we consider the world, the figure becomes 707,920,000 barrels.

BENEFITS FROM RESEARCH

We reluctantly turn aside from the fascinating story of gasoline and other fuels to consider briefly the benefits to the public through research in lubricants, so closely associated with fuels and so necessary wherever we find moving parts in a mechanism. Lubricants have been improved no less than the fuels, and no less importantly. The discovery of inhibitors against the oxidation of gasoline was also important to the lubricating oils in use; and, if improved design of engines has required more of the fuel, it certainly increased the burden upon the lubricant—which has been met, for example, by extreme-pressure lubricants and other types essential to successful operation on a growing number of instances.

It is only recently that lubricating oil has been the subject of intensive research study; but already the industry, largely abandoning the old sulfuric-acid method of refining, is now adopting the modern solvent-refining methods capable of yielding oil of exceptional stability, and at the same time lowering manufacturing costs. Whereas, previously unstable fractions were lost to sludge, all the oil is now recoverable; and even the rejected fractions have been found to contain valuable hydrocarbons of the unsaturated, or aromatic, type which may soon find their own place in commerce as the starting point of chemical synthesis. The development of propane and similar de-asphalting methods has made possible the employment, for lubricating oil manufacture, of crudes which might otherwise be regarded as too low in grade for anything except fuel oil. This is equivalent, obviously, to an increase in our supply of high-grade crude oils. The application of solvent and similar dewaxing methods has resulted also in an increased supply of lubricating oil of adequately low solidifying temperature with consequently improved lubrication in cold weather, with easier engine starting, and less cold weather wear of engine parts.

Solvent-refining methods both for improving oxidation stability and viscosity-index characteristics, as well as for removing waxes, have been rapidly developed; but research has also shown the possibility of obtaining similar results by the addition of certain synthetic substances for reducing the pour point of petroleum oils which permit the attainment of the desired low-temperature fluidity without resorting to expensive very low-temperature dewaxing, and at the same time preserves in the oil all its desirable characteristics. At present research continues in the attempt to improve the viscosity-temperature susceptibility characteristics, or fluidity at low temperatures, by addition of various types of heavy synthetic oil. Corrosion inhibitors have been important factors in improvements in oils.

[*Continued on page 541*]

The Catalytic Polymerization of Butylenes by Sulfuric Acid

S. H. McALLISTER
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CONTINUED improvements in automobile and airplane engines have called for "tailored fuels" of high octane number. These fuels are obtained by the polymerization of the lower olefins found in Dubbs pressure distillate. The Shell Companies have been producing *iso*octane from *iso*butylene in commercial scale for some time. Increasing demands for fuel having an octane number of 97 or better have led to the development of a modification of the original *iso*octane process. This method uses hot sulfuric acid as a catalyst; a portion of the normal butylenes is polymerized along with the *iso*butylene.

Almost double the yield of octenes is obtained from the same fuel stock and these, when hydrogenated, have an octane number nearly equivalent to that of pure *iso*octane. The process is in full commercial operation.

This paper was presented at Eighteenth Annual Meeting, American Petroleum Institute, Chicago, November 12, 1937.

INTRODUCTION

CONTINUED improvements in automobile and airplane engines have called for "tailored fuels" of very high anti-knock rating. The major source for such fuels lies in the polymerization of the lower olefins, and today there are a number of different types of commercial polymerization units in operation. The potential production of polymer gasoline has been estimated as over a billion gallons per year; and the advantages, both from an economic and conservational standpoint, have already been pointed out by Dunstan,[1] Egloff,[2] and Ipatieff,[3] and others.

The broad field of polymerization and the relative advantages of the various methods will not be reviewed here. This discussion is confined to processes for the production of an octane fuel having an octane rating of 98 to 100 from the C_4 fraction obtained from the Dubbs process.

The Shell Companies have been producing *iso*octane in commercial quantities by two methods which have been developed by them. The feed stocks used vary at different refineries, but a C_4 fraction containing 18.5 percent *iso*butylene and 28 percent normal butylenes might be chosen as representative of that available at a California refinery. The first commercial process used in the spring of 1934 was a cold-acid process.

COLD SULFURIC-ACID PROCESS

The processing unit Figure 1 consists of two sections: an absorption section and a polymerization section. The liquid hydrocarbon is contacted with 60 to 70 percent sulfuric acid at 20 to 35° C. countercurrently in two stages. Under these conditions the *iso*butylene, which is the more reactive of the olefins, is selectively absorbed into the acid phase. The absorption is an equilibrium reaction, and the amount of *iso*butylene absorbed depends upon:

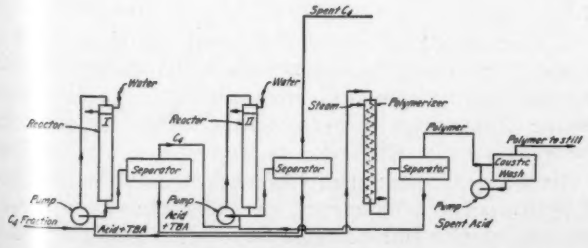

FIGURE 1
Cold-Acid *Iso*octane Plant

1. *Acid strength:* The stronger the acid, the more complete is the absorption of the *iso*butylene below limits where polymerization occurs. However, if the absorption is to be selective for *iso*butylene, acids of less than 70 percent strength should be used or the normal butylenes will also be absorbed.

2. *Acid-to-alcohol ratio in the acid phase:* The higher this ratio, the more complete the absorption.

3. *Temperature:* The lower the temperature, the more complete the reaction. However, temperatures above 20 and below 40° C. are preferable if a high reaction rate is to be obtained without premature polymerization.

Under the proper operating conditions it is possible to absorb up to 90 percent of the *iso*butylene without appreciably absorbing the normal butylenes.

The acid phase, after it has reached the desired degree of saturation with *iso*butylene, is separated off from the hydrocarbon phase and passed through a separate polymerization unit consisting of coils heated to 100° C. The reaction is complete in about a minute, and the products are stratified—the acid being returned to the absorption unit, while the polymer is washed and distilled. With 65 percent acid the polymer averages about 75 percent di*iso*butylene, the rest being trimers. With weaker acids a higher dimer content is obtained. After mild hydrogenation of the di*iso*butylene cut, *iso*octane (2,2,4-trimethyl pentane) is obtained.

This cold-acid two-stage process has been in use

TABLE 1
Comparative Efficiency, Cold-Acid and Hot-Acid Operation

	Cold Acid 65 Percent 30-35° C.	I 65 Percent Acid 80° C.	II 65 Percent Acid 90° C.
Fuel Composition:			
*Iso*butylene, percent by weight	18.5	18.5	9.1
*n*Butylene, percent by weight	28.0	28.0	20.6
Butanes, percent by weight	53.5	53.5	70.3
Products:			
*Iso*butylene, percent	2.4	0	0
*n*Butylenes, percent	26.6	15.1	11.4
Butanes, percent	53.5	53.5	70.3
Polymer, percent	17.5	31.4	18.3
*Iso*butylenes polymerized, percent	87	100	100
*n*Butylenes polymerized, percent	5	46.0	44.5
Total olefins polymerized, percent	37.5	67.5	61.5
Composition of Polymer:			
Sulfur (ASTM), percent	0.01	0.03*	0.062*
Octenes, percent	75	88	92
Octane rating of hydrogenated octenes	100	99.2	98.8

* Negligible sulfate esters present.

for some time, and is still the most suitable method of preparing pure *iso*octane. However, on the basis of the total olefins present in the C_4 fraction, the yield of octanes is relatively low; not more than 67 percent of the *iso*butylene is converted to *iso*octane; i. e., less than 26.7 percent of the total olefins in a feed stock containing 46.5 percent olefins. Increasing demands for polymer of 98 to 100 octane number has led to the development of the present hot-acid process, in which almost twice the yield of octanes may be obtained from the same feed stock.

HOT-ACID POLYMERIZATION

The hot-acid polymerization process was a direct outgrowth of the former process. When the temperature of the acid absorption reaction is raised, the absorbed *iso*butylene present in the acid phase condenses to polymer, and this is re-absorbed into the hydrocarbon phase. At temperatures above 60° C. this polymerization is sufficiently rapid that the absorbed *iso*butylene has only a transitory life in the acid phase, and the process becomes truly catalytic. The net effect of this is to force the absorption reaction to completion by maintaining the acid phase in a spent state. Thus it is possible to recover all of the *iso*butylene as polymer.

Raising the temperature also has the effect of reacting a portion of the normal butylenes, and these are absorbed into the acid layer principally in the form of acid sulfates. While the normal butylenes do not polymerize with themselves as readily as does *iso*butylene, in the presence of *iso*butylene they will react rather rapidly to form interpolymer. Thus, under proper operating conditions, it is possible to react up to an equal quantity of normal butylenes and *iso*butylene and, as the interpolymer on hydrogenation has an octane number nearly equal to that of pure *iso*octane, nearly double the yield of polymer is obtained without seriously sacrificing octane rating.

Besides the favorable effect on the olefin absorption, hot-acid operation has a further advantage in that polymer as formed passes into the hydrocarbon phase, and is diluted by the inert butanes; its activity is thereby reduced, and there is less opportunity for trimer formation or re-arrangement to polymers of lower octane number. The result is that the polymer is 85 to 90 percent octenes as against 75 to 80 percent for the old or cold absorption process. A comparison of the efficiency of the two processes is shown in Table 1. The increased yield of octenes is readily apparent.

LABORATORY INVESTIGATIONS

The results obtained by the process are dependent upon the mechanical system used, as well as upon chemical factors, such as acid strength and temperature.

A number of experimental reaction systems has been studied. These consisted of packed towers, heated coils through which the reactants were rapidly passed, a re-actor employing jet injection of the hydrocarbon into towers containing acid and a single mixer-type reactor. This latter arrangement, shown in Figure 2, proved to give the best results.

In this system the incoming feed is diluted with a much greater volume of the acid-hydrocarbon emulsion which contains practically no unreacted *iso*butylene. Thus the ratio of *iso*butylene to normal butylenes is very low, and interpolymerization is greatly favored; whereas in the coil or tower reactors co-polymerization of the *iso*butylene is favored owing to its higher initial concentration and much greater reaction rate.

Using the mixer type of reactor, the effect of the several variables in the reaction was experimentally determined. It was found that:

1. The effects of temperature and acid strength are closely interrelated. Acids ranging between 63 to 72 percent by weight can be used at temperatures from 75 to 100° C., the higher acid strength being used with the lower temperatures. It is preferable not to use stronger acids or higher temperatures, as formation of sulfur dioxide or sulfate ester will then become appreciable. Lower acid strengths lead to longer contact times and enhanced corrosion of the reactor system. However, within the above range, considerable flexibility is allowed without appreciably altering the results which are obtained.

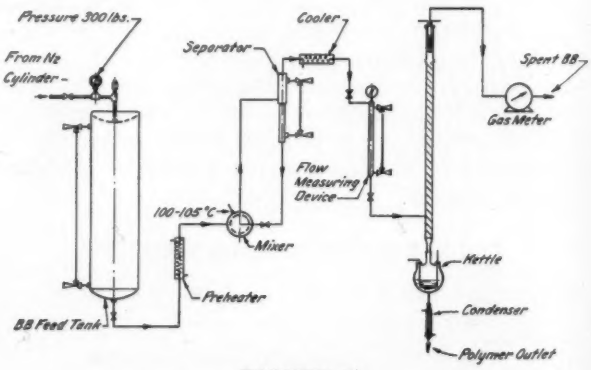

FIGURE 2
Experimental Hot-Acid Polymerization Plant

2. The size of the acid phase also affects the reaction. The larger the acid phase, the more rapid is the reaction. However, for commercial operation in the above limitations of acid and temperature, there seems to be little advantage in using more than a 1:1 or up to 2:1 ratio of acid to hydrocarbon.

3. The effect of increasing contact time is to increase the amount of reaction until an equal quantity of *iso*butylene and normal butylene is reacted. Above this, large increases in contact time increase the yields only slightly.

By using combinations of these variables, it is possible to react 90 percent of the *iso*butylene and 10 percent of the normal butylene, or completely to react the *iso*butylene and an equal quantity of normal butylenes. This flexibility is an advantage when vola-

tility requirements in winter call for more butanes and butylenes.

COMPOSITION OF THE ACID PHASE

The sulfuric acid used in the process functions as a catalyst, and contains relatively small amounts of organic materials. It is used for weeks or months without change, fresh acid being added from time to time merely to make up for that lost by mechanical entrainment. The chemical consumption cost is, therefore, very low.

LARGE-SCALE APPLICATIONS

The laboratory results were directly translated to full commercial-scale plants with the predicted yields. The Martinez polymer plant is shown in Figure 3. The reactor unit resembles a single stage of the cold-acid process. In fact, the equipment is largely interchangeable. In the plant the fresh feed meets re-cycling emulsion, and the mixture is then rapidly re-cycled through a heat exchanger and time tanks. A portion of the emulsion is continuously withdrawn to a separator, where the acid is separated and returned to the reactor, while the hydrocarbon is worked up for the polymer.

The operation of the unit is extremely simple—one operator per shift being sufficient. No external

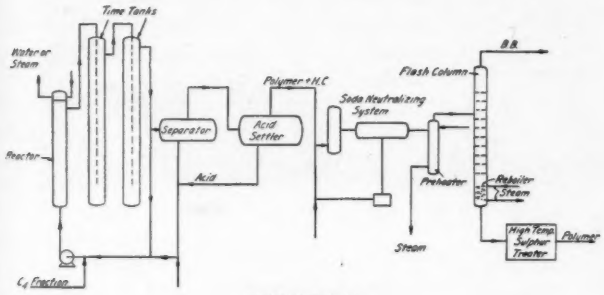

FIGURE 3
Flow Diagram, Hot-Acid Polymerization Plant

heat is required, as the exothermic heat of reaction is sufficient to maintain the temperature in the reactor. The return of the acid to the reactor is largely automatic, once the rate of flow is established. In present practice 67 percent acid is used at approximately 80° C., and a 10- to 15-minute average contact time is allowed.

POLYMER RECOVERY SYSTEM

As has already been pointed out, the polymer in the hot-acid system is recovered from the hydrocarbon layer. This recovery consists of a caustic wash to remove entrained acids or acid sulfates, a flash tower to strip off the spent hydrocarbon gases, and a high-temperature treater for further sulfur removal. This latter unit serves the valuable purpose of removing the stable sulfate esters which are present in the polymer to the extent of 0.2 to 0.4 percent calculated, ASTM sulfur.

After treatment less than 0.03 percent sulfur remains, and sulfate-ester removal is substantially complete. The polymer is thus rendered stable to distillation, or it could be added directly to gasoline without impairing its color or stability.

A distillation curve of the crude polymer obtained from the treater is shown in Figure 4. It will be seen that the entire product could be added to gasoline, and the boiling range of the octene fraction is very narrow.

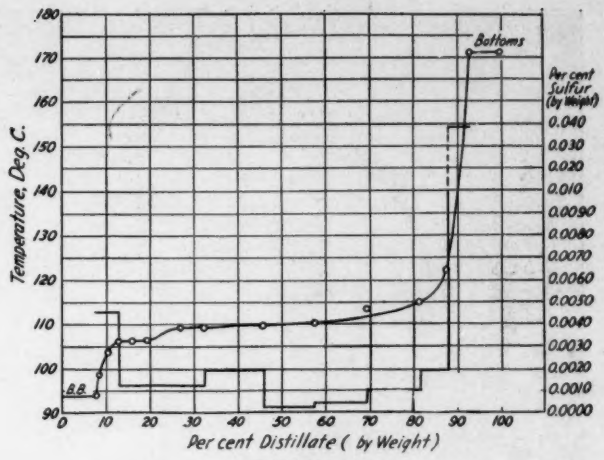

FIGURE 4
Martinez Polymer "Precision" Distillation, Emeryville, Calif.

The octene fraction is refractionated and hydrogenated under mild conditions. The product obtained averages 98 to 99 octane number. Thus, as already pointed out, by hot-acid operation the yield has been doubled without sacrifice of octane number.

Tables 2, 3 and 4 are set out to show a comparison

TABLE 2
Comparison of Hot-Acid Octane with Technical *Iso*octane

	Hot-Acid Octane	Technical *Iso*octane
Reid vapor pressure, lb. per sq. in.	2.3	2.1
Color, Saybolt	30+	30+
API gravity, deg.	66.5	70 9
Olefin, percent	1.5	1.8
Copper-dish gum, mg. per 100 cc.	1	1
Accelerated aging test, mg. per 100 cc.	1	1
Wright acid heat, deg. F.	24	23
Navy acid heat, deg. F.	3	3
ASTM Distillation, Deg. F.:		
Initial boiling point	208	205
Dry point	238	235
10-percent point	222	210
20-percent point	224	210
30-percent point	225	210
40-percent point	226	211
50-percent point	226	212
60-percent point	227	212
70-percent point	227	212
80-percent point	228	214
90-percent point	229	215
95-percent point	231	216
Distilled, percent	99	99
Sulfur (Nephelometric), percent	0 0001	0 .0001

TABLE 3
Anti-knock Blending Octane Numbers

Aviation Base Stock (Percent)	Hot-Acid Octane (Percent)	Technical *Iso*octane (Percent)	Octane No.
100	...	...	74.3
75	25	...	79.1
75	..	25	79.3
50	50	..	84.8
50	..	50	85.2
25	75	..	90.9
25	...	75	91.0
0	100	...	99.1
0	..	100	99.7

NOTE.—100 percent hot-acid octane and 100 percent technical *iso*octane were matched against one another in an engine, and hot-acid octane is found only slightly lower.

TABLE 4
Lead Susceptibility—50 Percent of Aviation Base Stock and 50 Percent of Octanes

Tetraethyl Lead (CC. Per Gal.)	Blend with Hot-Acid Octane	Blend with Technical *Iso*octane
0.0	84.8	85.2
1.0	94.6	94.6
2.0	97.0	97.1
3.0	98.7	99.1

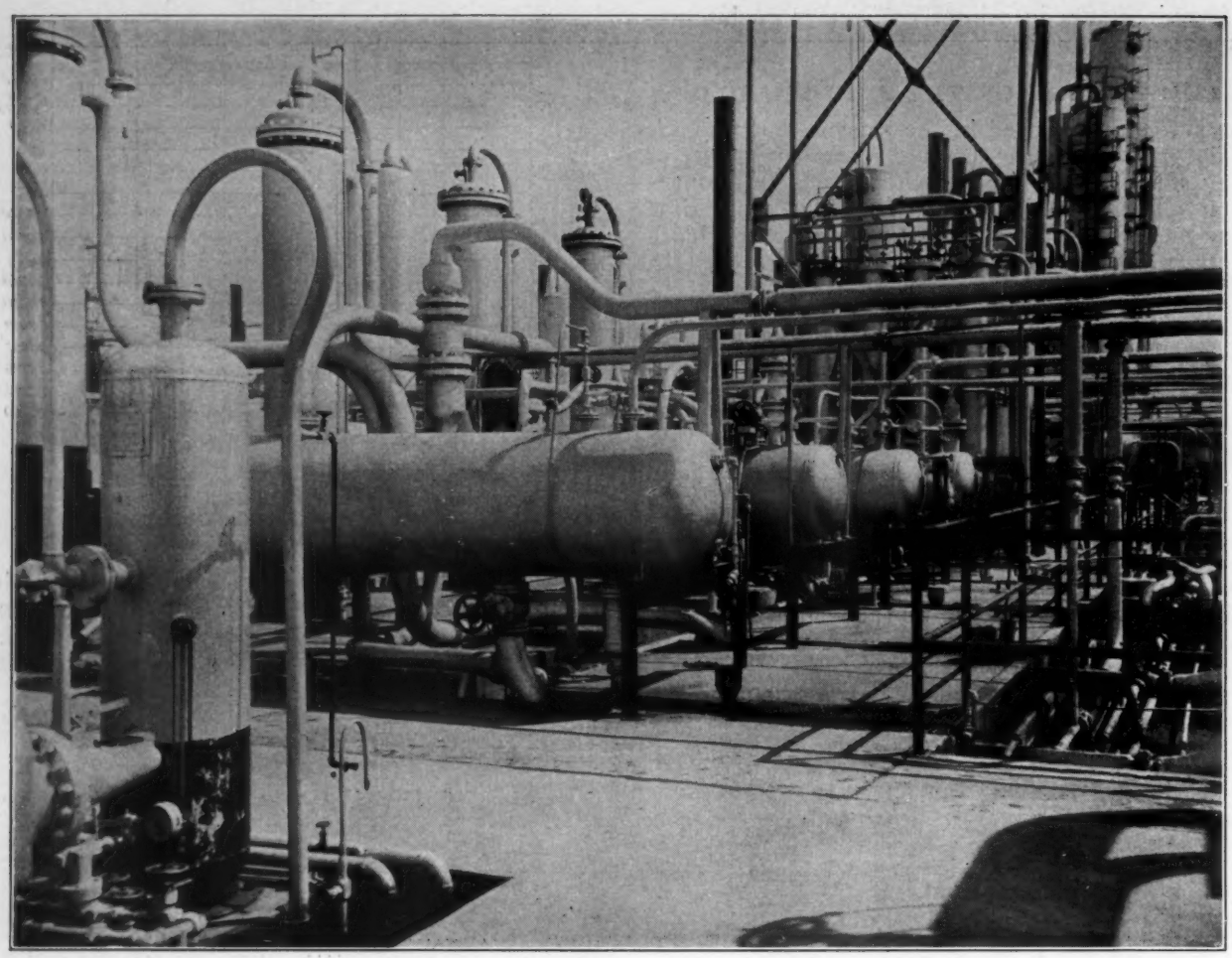

FIGURE 5

between pure *iso*octane and hydrogenated interpolymer prepared by this process.

Corrosion: One question which is of importance in commercial applications is that of corrosion through the use of sulfuric acid at these temperatures. No special alloys are used in any of the plants. The reactors themselves are of mild steel, and the pumps are of standard design. Iron or steel tubing is used throughout. Copper and bronze could also be used, but stainless steel shows very poor service. In one refinery, reactors, which had previously seen considerable service under the conditions of the cold-acid process, have been in continuous use on the hot-acid process for 18 months, and are still giving good service. With proper design and reasonable care, maintenance costs are very low. Evidence indicates that wear results as much from erosion as from corrosion, and in any case these are not serious factors when considering a plant of this type. The major cost in a polymer plant is in the distilling and auxiliary equipment, which is common to any catalytic process. The reactor unit itself is relatively inexpensive.

PATENTS

Various features of these processes are covered by patents and pending applications in the United States and abroad.

CONCLUSION

From the foregoing it is apparent that the hot sulfuric-acid process as operated by the Shell Companies is particularly applicable to the polymerization of the C_4 fraction when octanes of 98 to 100 octane number are desired.

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Motor Fuels from Polymerization

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1. The polymerization process is one of the most important developments in the petroleum refining industry. More than 9,000,000,000 gallons of polymer gasoline may be produced yearly from the hydrocarbon gases in the United States, of which more than 1,000,000,000 gallons may be *iso*octane fuel of 95 to 100 octane rating.

2. Three modifications of the polymerization process have been described: *a*, polymerization of hydrocarbon gases containing propane and butene; *b*, Pyrolytic cracking of butanes (and also propane) to produce olefin hydrocarbons followed by catalytic polymerization to produce polymer gasoline; *c*, selective polymerization of normal and *iso*butene and hydrogenation of the resulting octenes into *iso*octanes.

3. A commercial plant has been described processing daily 13,070,000 cubic feet of cracked gas containing 19.2 percent of propene-butenes, polymerizing 79.5 percent of these olefins, and producing 1,080 barrels of true polymer in addition to 974 barrels of butanes. When treating a cracked gas containing 25.4 percent of propene-butenes at the daily rate of 13,874,000 cubic feet, a total of 1,474 barrels of true polymer was produced and 1,152 barrels of butanes. The percentage of propene-butenes polymerized was 86.5 percent. In another commercial plant, treating approximately 1,500,000 cubic feet of gas per day, containing 38 percent propene-butenes, the production was 250 barrels of polymer gasoline with a polymerization of 89 percent of the propene-butenes present.

4. A commercial plant, comprising a combination butane-cracking and catalytic - polymerization process, charges butane at the daily rate of 1,090 barrels, producing 402 barrels of polymer gasoline made up of 109 barrels of pyrolytic polymer and 293 barrels of catalytic polymer gasoline.

5. A commercial plant has been described treating butane-butene mixtures selectively to polymerize the normal and *iso*butenes contained therein, having a daily capacity of 1,300 barrels of butane-butene fractions, from which was produced 347 barrels of *iso*octenes. The *iso*octenes are catalytically hydrogenated to *iso*octanes, the latter having octane ratings of from 90 to about 100—dependent upon the conditions under which they are produced.

6. The economic position of the polymerization process for the production of polymer gasoline to improve the octane rating of the refinery output, or as a step in the process of making *iso*octanes, is now in relatively wide use in the oil industry.

This paper was presented at eighteenth annual meeting, American Petroleum Institute, Stevens Hotel, Chicago, Ill., November 12, 1937.

1. INTRODUCTION

THE polymerization process is one of the most important developments in the petroleum-refining industry. Motor fuel was first produced by straight distillation, and later by cracking. The quantity of gas produced in the cracking process increases with the improvement of the anti-knock quality of the motor-fuel product, and a satisfactory economic disposal of this gas was a real problem. This was solved by the introduction of the polymerization process with the production of a superior motor fuel from the gas. The cracking process depends for its economic utility on the conversion of heavier hydrocarbons to lighter ones of greater value, while the polymerization process is in principle the reverse, viz., the conversion of gaseous hydrocarbons to liquid ones in the form of high anti-knock motor fuel.

Over 9,000,000,000 gallons of polymer gasoline may be produced yearly from the hydrocarbon gases produced in the United States, of which over 1,000,000,000 gallons may be *iso*octane fuel of 95 to 100 octane rating. The principal economic goal of the polymerization process was the conversion of these gases used primarily for heating purposes into motor fuel. The objective was not only attained, but the product was found to be a super type.

The demands of the automobile and aircraft industries for high octane fuel have been increased from year to year; and polymerization in its various modifications and aspects, including selective polymerization for the production of *iso*octanes, has met these demands. Since 1925 the maximum automobile speed has increased from 60 to more than 100 miles per hour, and the cruising speed of airplanes from 80 to 220 miles per hour—and this has been made possible primarily by high octane motor fuels.

The requirements of automobiles may generally be satisfied by fuels of a value less than 75 octane. For airplanes, however, fuels of 95 to 100 octane are desirable, and for military purposes are necessary. The Army and Navy have practically set a standard of 100-octane fuel for their own use, and will require from 50,000,000 to 60,000,000 gallons for the current year. The diplomacy of European and Far-Eastern countries is built up around petroleum, the most important strategic product of which is 100-octane aviation fuel.

The power output and load-carrying capacity of a given airplane has been increased. When using a 100 octane fuel, an increase in power of from 20 to 30 percent over that of an 87-octane fuel was obtained.

Polymerization has pointed the way, and is a definite advance, in chemical control of the composition and properties of motor fuels. The day has arrived when a motor fuel may be designed and produced commercially as branch-chain paraffins such as *iso*octanes or mixtures of *iso*octanes, *iso*pentanes, and *iso*hexanes.

For many years it has been the goal of chemists in

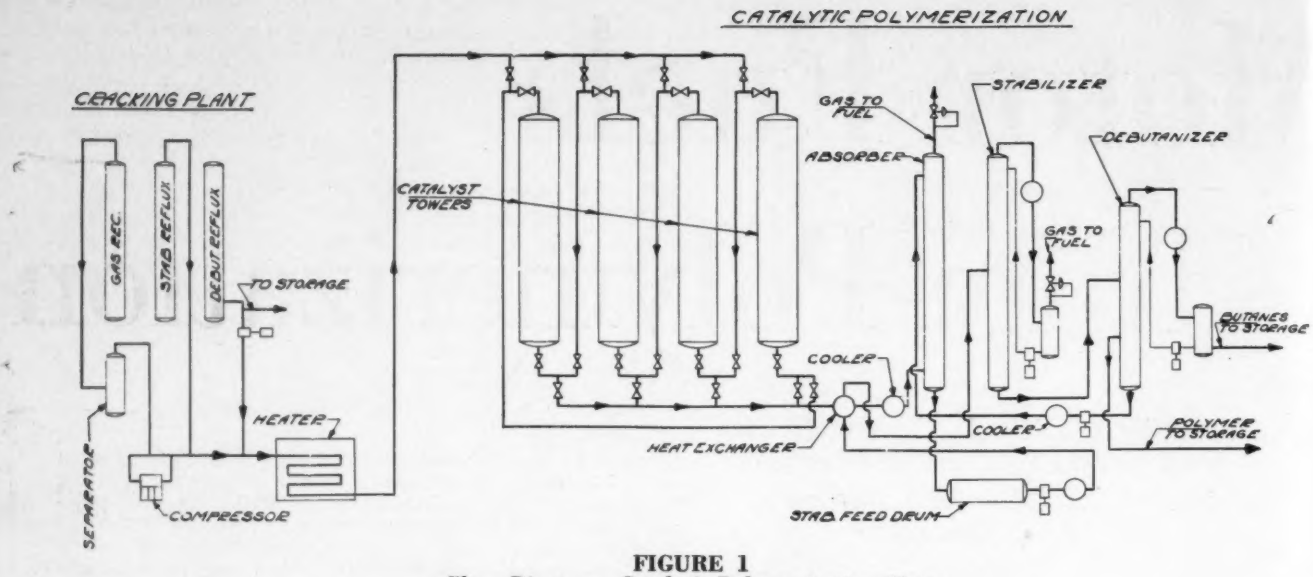

FIGURE 1
Flow Diagram, Catalytic-Polymerization Unit.

the petroleum industry to employ petroleum as a raw material for the production of chemical derivatives of petroleum hydrocarbons for use in the various arts and industries. This goal is now a reality because of the development of the cracking process whereby the olefins contained in the gases produced therefrom may be converted into a large number of products including alcohols, glycols, alcohol ethers, ethers, oxides, aldehydes, ketones, esters, acids, anhydrides, chlorinated compounds, amines, and products useful in the arts as explosives, dyes, medicinals, and the like.

The catalytic polymerization process represents one of the most important steps in the production of these chemical derivatives in addition to providing a chemical means for the petroleum technologist to produce motor fuels, such as *iso*octanes, having definite composition and properties.

In the present report three modifications of catalytic polymerization will be described. All of them employ the so-called solid phosphoric-acid catalyst developed by V. N. Ipatieff.

One of the simplest means of utilizing the catalytic polymerization process is to treat gases containing propene and butenes. In the first modification to be described in this paper, the charging material consists of hydrocarbon gases containing propene and butenes. In the second modification, known as the "selective polymerization process," the olefins contained in the hydrocarbon gases are principally butenes. In the third process to be described, the paraffin hydrocarbons such as butanes are converted by pyrolysis into olefin hydrocarbons which are subsequently converted into motor fuel by catalytic polymerization.

2. CATALYTIC POLYMERIZATION

A catalytic-polymerization unit in commercial operation, treating 14,000,000 cubic feet of cracked gas a day containing 25.4 percent of propene and butenes in producing at the daily rate of 68,000 gallons of 82-octane motor fuel of 9 to 10 pounds Reid vapor pressure.

TABLE 1
Analysis of Gas Leaving Cracking-Plant Receiver

	Mol Percent
Methane	58.20
Ethylene	6.71
Ethane	13.09
Propene	6.05
Propane	10.62
Butene	2.06
Butanes	2.08
Pentanes and heavier	1.19

The gas to be treated is obtained from the stabilizer and the debutanizer of the cracking unit and may, if desired, include the gas from the receiver.

Typical analysis of the gas leaving the cracking plant receiver is shown in Table 1.

The unstabilized gasoline produced in the cracking process is pumped to a stabilizer, operated at a pressure of 350 pounds, to produce propane-propene free bottoms. In this operation part of the butane-butene fraction is taken over at times.

An analysis of the gas from the stabilizer is shown in Table 2.

TABLE 2
Analysis of Gas from Stabilizer

	Mol Percent
Methane	11.01
Ethylene	5.98
Ethane	19.10
Propene	18.38
Propane	35.67
Butenes	4.89
Butanes	4.97

The gasoline from the stabilizer may go direct to storage or may pass to a debutanizer, operated at a pressure of about 100 pounds, wherein the cracked gasoline is stabilized to a low vapor pressure. This vapor pressure is determined by the over-all yearly butane balance of the plant. The butane-butene fraction may go to storage or part of it may go to the polymerization unit.

Various proportions of the gases from the cracking unit obtained as described are charged to the polymerization unit at a pressure of approximately 300 pounds. The combined charge to the polymerization unit is heated to a temperature of 375-400°F., and is passed through the catalyst towers in series flow. The towers are packed with the solid granular phosphoric-acid catalyst, which has a definite size and shape. When passing through the catalyst towers, the gases increase in temperature about 150°F. due to the exothermic polymerization reaction. The rise in temperature varies

with the percentage of higher olefins in the gas being processed.

Analyses of hydrocarbon gases charged to the catalytic-polymerization unit at various times during the operation are shown in Table 3.

TABLE 3

Analysis of Hydrocarbon Gases Charged to Polymerization Unit

	(1) Mol Percent	(2) Mol Percent	(3) Mol Percent
Methane	13.9	24.1	32.3
Ethane and ethylene	21.7	24.6	23.3
Propene	15.4	12.8	12.8
Propane	32.5	25.0	20.2
Butenes	8.5	6.2	5.4
Butanes	8.0	7.3	6.0

A typical flow sheet of this process is shown in Figures 1 and 2. The mixed gases are passed through a heater, wherein they are raised to the reaction temperature; and are then passed under the oprating pressure of the polymerization process through the catalyst towers. The towers are arranged so that they may be operated in sequence and so that any one of them may be cut out for regeneration.

The polymer product, together with residual gas, passes through heat exchangers and coolers into an absorption column, operated at a pressure of 225 pounds, employing the low-vapor-pressure fraction of the polymer as an absorption oil. The liquid product from the absorber passes to a stabilizer feed drum, and the residual gas goes to the fuel system. The liquid in the stabilizer feed drum is heat-exchanged with the products leaving the catalyst tower, and is then fed into the stabilizer—the gases from which are passed to the fuel system, or they may be re-circulated back to the catalyst towers. The overhead from the stabilizer contains propane-propene and lighter gases. The liquid product from the stabilizer flows to the debutanizer, operating at 100 pounds pressure, wherein the C^4 fraction containing about 13 percent butenes is removed and sent to storage. The polymer product is removed as a side cut from the debutanizer and sent to storage, and the low-vapor-pressure polymer from the bottom of this column is recirculated as absorption oil.

As the run progresses, the order in which the catalyst towers are used is changed. During the operation the catalyst becomes covered with a carbonaceous deposit which reduces its catalytic activity and which must be removed periodically. The tower containing the catalyst which has become inactive is cut out of the system, and the catalyst regenerated by controlled oxidation. After burning, a steam treatment is used to re-hydrate the catalyst which otherwise would be inactive. The catalyst in each tower is reactivated after being in service about 60 days.

From the operation to date, a total polymer produc-

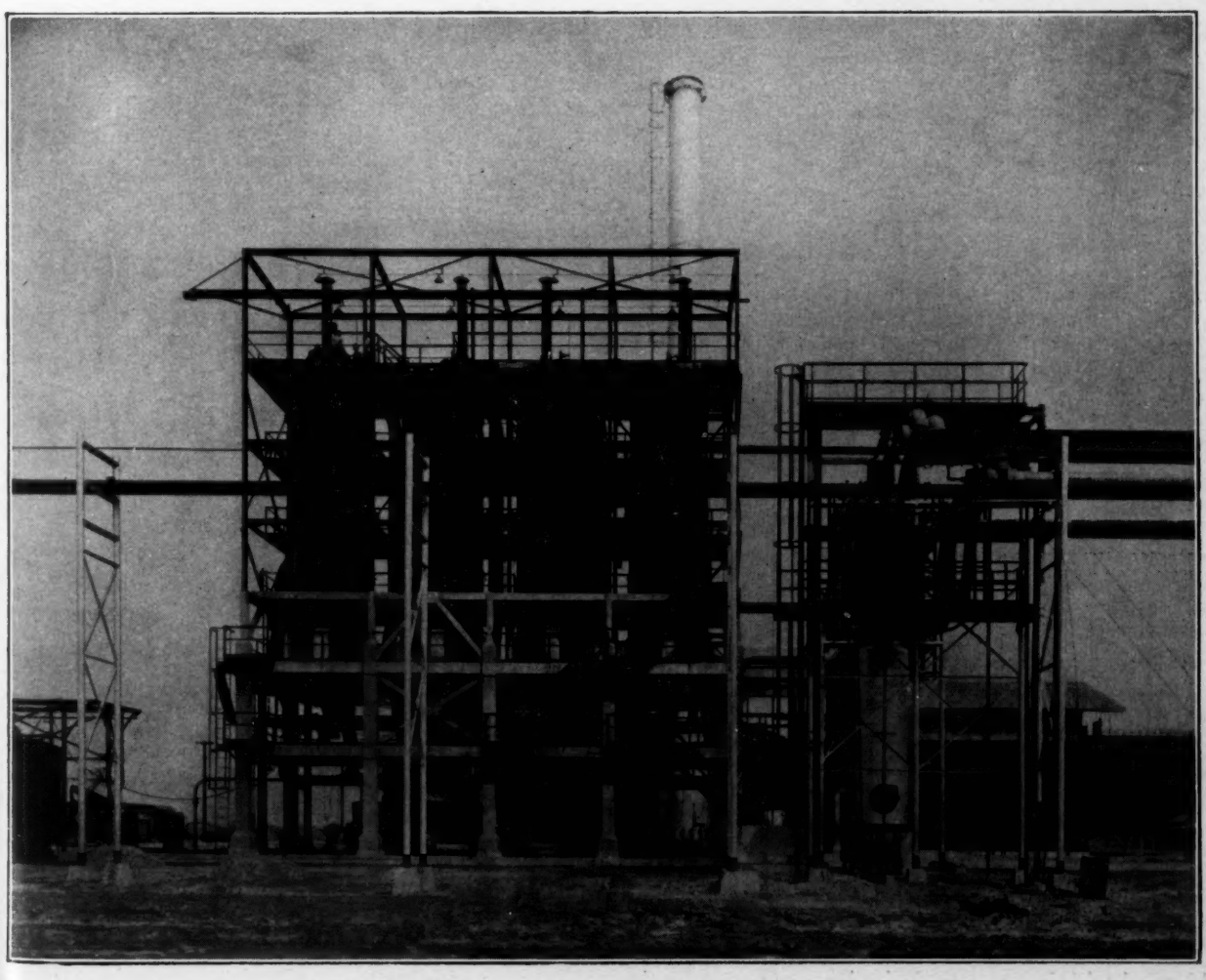

FIGURE 2
Catalytic-Polymerization Unit.

TABLE 4
Analysis of Gas Leaving Absorption Column

	(1) Mol Percent	(2) Mol Percent	(3) Mol Percent
C1	33.2	42.6	55.6
C1	42.3	33.6	28.5
C1	22.9	22.2	15.1
C1	1.6	1.6	0.8
Propene and butenes	3.3	5.0	2.8

tion equivalent to about 50 gallons per pound of catalyst has been obtained without any apparent appreciable change in the activity of the catalyst.

Typical analyses of the gas leaving the absorption column at various times during the operation are shown in Table 4.

TABLE 5
Analysis of Stabilizer Gas to Fuel System

	Mol Percent
Methane	4.4
Ethane and ethylene	27.4
Propene	7.0
Propane	61.0
C1+	1.2

An analysis of the stabilizer gas (depropanizer) to the fuel system is shown in Table 5.

TABLE 6
Analysis of Polymer Product

Gravity, deg. API	62.2
ASTM Distillation, Deg. F.:	
Initial boiling point	162
10-percent point	189
20-percent point	197
50-percent point	226
80-percent point	290
90-percent point	332
End point	435
Recovery, percent	98.5
Residue, percent	1.0
Loss, percent	0.5
Reid vapor pressure, lb.	2.7
Octane No.	82.0

The polymer product of the process has a Reid vapor pressure of 2 to 3 pounds, and other properties are shown in the analysis in Table 6.

The polymer may be sweetened and blended directly with gasoline, or may be re-distilled if a water-white product is desired.

When the product is re-distilled, doctor-sweetened, and blended with butanes to desired vapor pressure, the analysis is as shown in Table 7.

TABLE 7
Re-drilled Polymer Product

Gravity, deg. API	67.1
ASTM Distillation, °F.:	
Initial boiling point	95
10-percent point	156
20-percent point	186
30-percent point	200
40-percent point	212
50-percent point	221
60-percent point	233
70-percent point	250
80-percent point	280
90-percent point	329
End point	376
Recovery, percent	95.5
Residue, percent	0.5
Loss, percent	4.0
Reid vapor pressure, lb.	10.8
Color	30
Doctor test	O.K.
Corrosion test	O.K.
Induction period, min.	135
Copper-dish gum, mg. per 100 cc.	6
Sulfur, percent	0.199
Octane No.	82.0

A typical daily operating summary showing quantities charged and yields of products is shown in Tables 8 and 9. Tables 8 and 9 show the results of catalytic processing of cracked gas containing 19.2 and 25.4 percent propene-butenes, respectively.

In another commercial installation shown in Figure 3, the gas for polymerization is taken from the cracked-gasoline stabilizer at a pressure of about 190 pounds and a temperature of 135°F. The gas from the stabilizer contains from 35 to 40 percent of propene and butenes. The hydrogen-sulfide content is relatively high, and contains from 2 to 2.5 percent hydrogen sulfide. If the gas containing hydrogen sulfide is passed through the catalytic-polymerization unit, the gasoline formed would contain about 2 percent sulfur, mostly of the mercaptan type, which would be formed during the reaction. Doctor-sweetening the polymer gasoline would be somewhat difficult, and there would be a loss in octane number during the sweetening operation.

TABLE 8
Catalytic Processing of Cracked Gas—Propene-Butene

	1,000 Cu. Ft.		Propene-Butenes (Percent)	
Total Feed to Plant	13,070		19.2	
Gases from Plant:				
Absorber gas	6,700			
Stabilizer gas	2,900			
Butanes to storage	1,350			
Total gas from plant	10,950		4.3	
Propene-butenes polymerized, percent		79.5		
Liquid Yield from Plant:		Bbl.		
Butanes to storage		914		
Butanes to blend		60		
Total butanes		974		
True polymer (2-3 lb. Reid vapor pressure)		1,082		
Re-run polymer		1,073		
Re-run bottoms		9		
True polymer, gal. per 1,000 cu. ft. of total feed				3.48

The removal of hydrogen sulfide is accomplished by passing the gas, which is available at about 190 pounds pressure and 135°F. temperature, through an absorber column. The absorber column is operated at a pressure of 180 pounds and a temperature of about 145°F. Under these conditions no condensation of the heavy hydrocarbons in the gas will take place.

TABLE 9
Catalytic Processing of Cracked Gas—Propene-Butene Content, 25.4 Percent

	1,000 Cu. Ft.		Propene-Butenes (Percent)	
Total Feed to Plant	13,874		25.4	
Gases from Plant:				
Absorber gas	5,062			
Stabilizer gas	4,032			
Butanes	1,624			
Total gas from plant	10,718		4.6	
Propene-butenes polymerized, percent		86.5		
Liquid Yield from Plant:		Bbl.		
Butanes to storage		1,064		
Butanes to blend		88		
Total butanes		1,152		
True polymer (2-3 lb. Reid vapor pressure)		1,474		
Re-run polymer		1,464		
Re-run bottoms		10		
True polymer, gal. per 1,000 cu. ft. of total feed				4.47

The gas enters the bottom of the absorber, and tri-potassium phosphate solution is pumped into the top of the column. The tri-potassium phosphate solution is regenerated and circulated. The gas leaving the top of

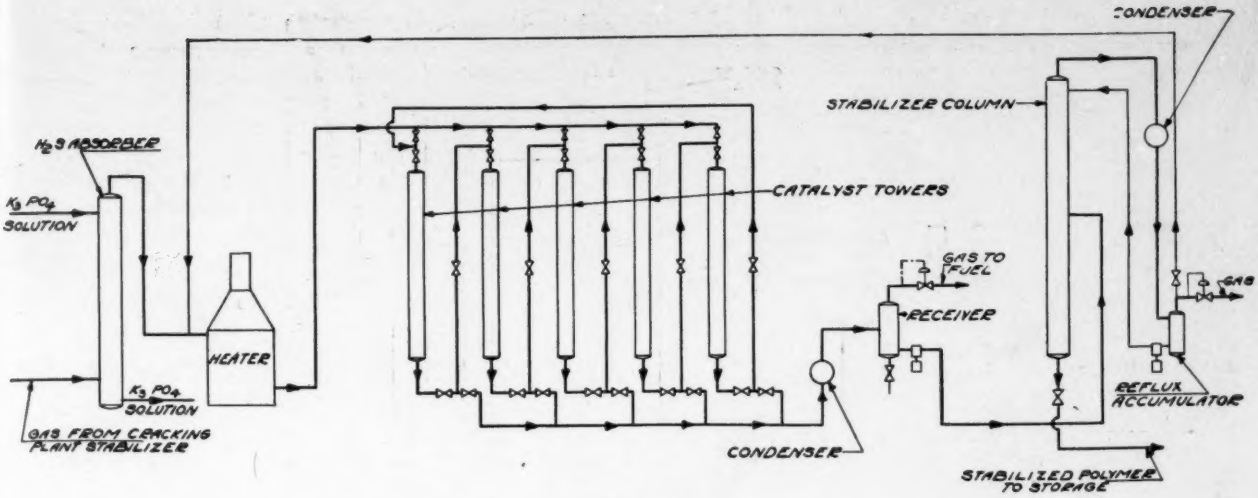

FIGURE 3
Flow Diagram, Stabilizer Unit.

the absorber has a hydrogen-sulfide content of the order of 0.10 percent.

The polymerization unit was designed to process 2,500,000 cubic feet of gas per day. At the present time there is about 1,500,000 cubic feet per day of gas available in this refinery for polymerization which contains about 40 percent higher olefins.

For the best operation of the polymerization unit, gas from the polymer stabilizer is re-cycled through the catalyst towers along with the fresh feed, so there is a charge of about 2,500,000 cubic feet per day through the polymerization unit. The propene-butene content of the combined charge to the polymer plant is about 29 percent.

The combined feed passes through the gas heater and enters the first tower at a temperature of about 400°F., and passes through the catalyst towers in series flow. The polymer and residual gas pass through the condenser and into the unstabilized-polymer receiver. The pressure is held on the entire system by the pressure-control valve on the gas release from the polymer receiver. This gas passes to the fuel system.

The polymer gasoline is then stabilized to the desired vapor pressure. The stabilizer is operated at a sufficiently high pressure so that a controlled quantity of the stabilizer gas can be charged back to the fresh feed as re-cycle without compressing. The net make of gas from the stabilizer is discharged to the fuel system.

The amounts of gas charged and yields of products are shown in Table 10.

TABLE 10
Gas Charge and Product Yields

	1,000 Cu. Ft. Per Day		Propene-Butenes (Percent)	
Fresh Feed to Plant	1,483		37.9	
Stabilized polymer gas	901		15.0	
Combined charge to plant	2,384		28.9	
Gases from Plant:				
Polymer receiver gas	753		3.4	
Stabilizer reflux accumulator gas	231		15.0	
Total gases from plant	984		6.1	
Propene-butenes polymerized, percent		89		
Total polymer produced, bbl.		250.5		
Polymer produced, gal. per 1,000 cu. ft. of total feed				7.1

The analysis of the polymer gasoline is given in Table 11.

3. BUTANE CRACKING AND CATALYTIC POLYMERIZATION

A combination gas cracking and catalytic polymerization unit for the conversion of butanes and polymerization of the olefins produced is in commercial operation processing 1,090 barrels a day of butane. The butane cracking at high temperature and pressure produces relatively large yields of olefin containing gases and relatively small amounts of pyrolytic gasoline. The cracked gases are polymerized catalytically as already described.

Referring to Figures 4, 5, and 6, butanes from the charge tank are pumped through a heater which operates at a pressure of about 750 pounds and a transfer temperature of 1065-1075°F. Sufficient soaking time is provided in the heater to produce the desired conversion of about 50 percent of the charge.

The transfer material is cooled to about 90°F. under full plant pressure, and is released into the demethanizer column which operates at 300 pounds pressure.

In this column substantially all of the methane and part of the ethane and ethylene are removed overhead, and the remaining components are removed as bottom product. This separation is accomplished by using debutanized pyrolytic polymer as absorption oil in the top of the column and partially stripping the liquid in the bottom of the column through re-boiling.

The bottom product from the demethanizer is discharged into the debutanizer column. This column is operated at sufficiently high pressure so that the over-

TABLE 11
Analysis of Polymer Gasoline

Gravity, deg. API	68.3
ASTM Distillation, °F.:	
Initial boiling point	87
10-percent point	132
50-percent point	209
90-percent point	325
End point	403
Recovery, percent	96.5
Residue, percent	0.5
Loss, percent	3.0
Reid vapor pressure, lb.	9.8
Octane No.	82.2
Mercaptan sulfur, percent	0.025
Copper-dish gum, mg. per 100 cc.	5

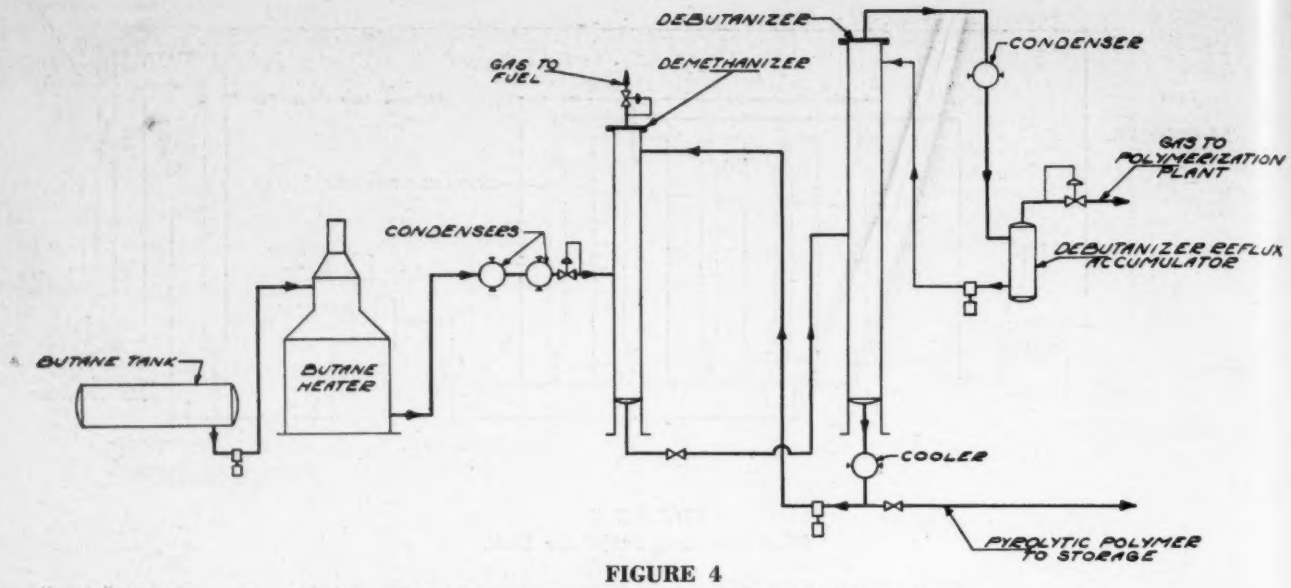

FIGURE 4
Flow Diagram, Butane-Cracking and Catalytic-Polymerization Unit.

head gases may be satisfactorily processed in a catalytic-polymerization plant. These overhead gases which include all of the butane-butenes and lighter hydrocarbons produced during the cracking reaction, with the exception of those discarded from the demethanizer column, contain from 25 to 28 percent of propene-butenes.

A debutanized pyrolytic polymer is removed from the bottom of the column. Part is re-circulated to the demethanizer column as absorption oil, and the remainder passes to storage.

The polymerization unit is of the same type already described. It is followed by conventional fractionation equipment for the separation of catalytic polymer of the desired vapor pressure, and residual butane.

It has been found advantageous to remove hydrogen sulfide from the butane before charging to the unit, since this results in the production of doctor-sweet products.

In a typical operation, the butane fraction from the natural gasoline plant used as charging stock for the cracking-catalytic polymerization unit showed the analysis in Table 12.

This charging stock at the rate of 1090 barrels per day was heated to a temperature of 1065°F. and 750 pounds pressure in the cracking unit, from which 109 barrels per day of pyrolytic polymer gasoline of 4.7 Reid vapor pressure was produced, having additional properties shown in Table 13.

The hydrocarbon gases from the debutanizer of the butane cracking unit were analyzed for their propene and butene content, which showed 27.7 percent. This gas was passed through the catalytic-polymer-gasoline unit, producing at the rate of 293 barrels per day based upon the original 1,090 barrels butane processed. The analysis of the polymer gasoline produced is shown in Table 14.

TABLE 12
Analysis of Butane Fraction

	Mol Percent
Propane	3.3
*n*Butane	83.2
*Iso*butane	12.2
Pentane	1.3

TABLE 13
Pyrolytic Polymer Gasoline

Gravity, °API	48.5
ASTM Distillation, °F.:	
Initial boiling point	119
10-percent point	147
20-percent point	159
50-percent point	202
90-percent point	407
End point	520
Reid vapor pressure, lb.	4.7
Octane No. (CFR method)	74
Sulfur, percent	0.22

4. SELECTIVE POLYMERIZATION AND *ISO*-OCTANE MOTOR FUEL

The catalytic production of *iso*octenes from the normal and *iso*butene present in cracked gases is being carried out commercially under relatively mild conditions. The *iso*octenes produced are hydrogenated into *iso*octanes of values ranging from 90 to about 100 octane. The octane ratings can be controlled as a function of the percentage of normal and *iso*butene present in the charge and of the time, temperature, and pressure conditions. The higher the octane rating, the lower the yield of *iso*octanes per barrel of butane-butene processed.

The process of producing *iso*octanes by the catalytic-polymerization reaction uses as a charging stock the butane-butene (B.B.) fraction from the stabilizer producing the vapor-pressure cracked gasoline desired. The B. B. fraction contains 15 percent of *iso*butene, 30 percent of normal butene, and 55 percent of normal and *iso*butanes. A flow chart of the *iso*octane process is shown in Figure 7.

The butane-butene charge is passed through a caustic-soda scrubber to remove the sulfur components present. The liquefied hydrocarbon gas is then pumped through a heating coil, wherein the temperature is raised to about 350°F. under a pressure of about 600 pounds. The B. B. fraction then passes through a "solid phosphoric-acid" catalyst, wherein the exothermic heat of the reaction is controlled by a cooling fluid, such as oil around the reaction tubes, and the desired temperature is maintained during the polymerization. Dependent upon the time-temperature-pressure conditions prevail-

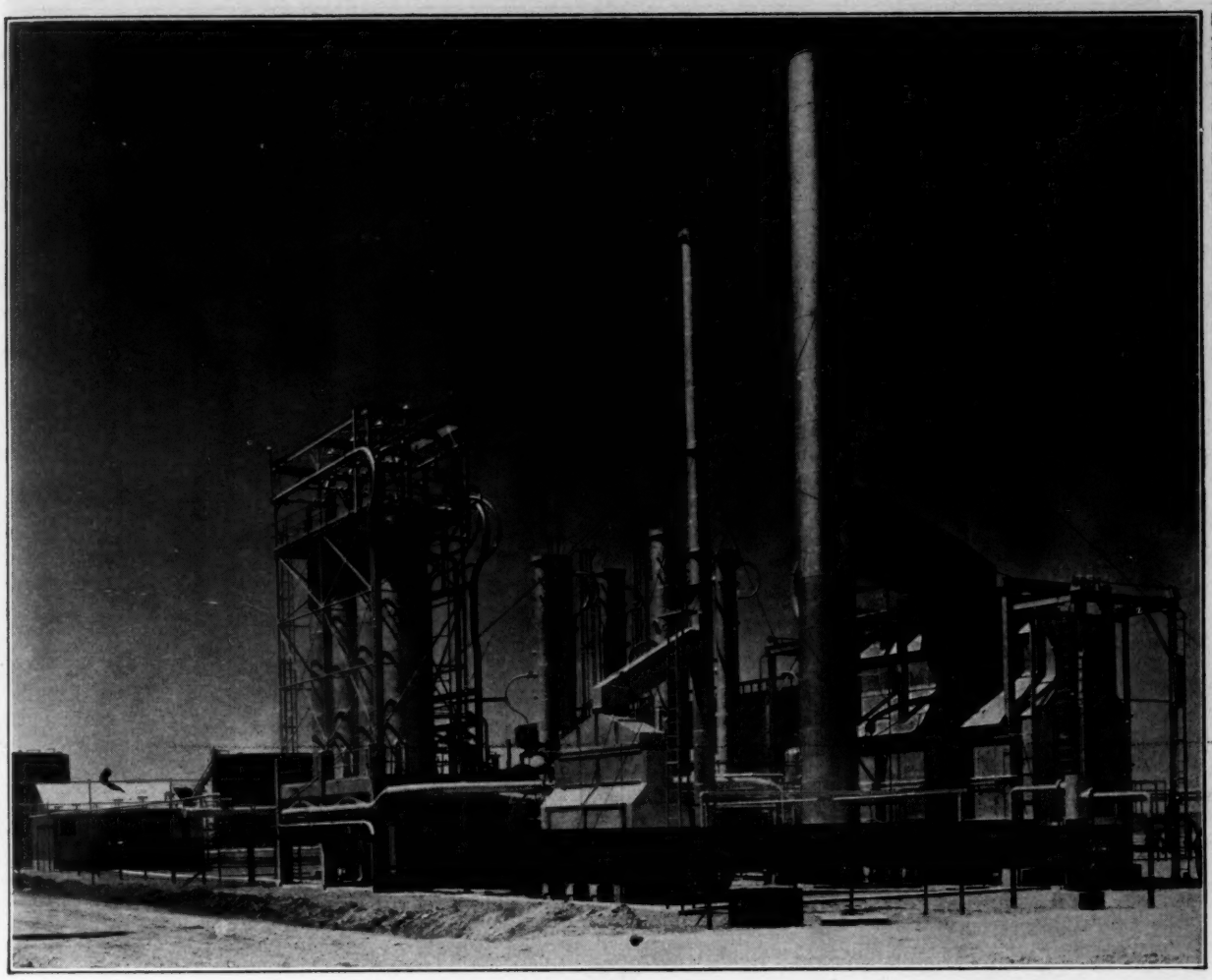

FIGURE 5
Butane-Cracking and Catalytic-Polymerization Unit (View 1).

ing and the percentage of normal to *iso*butane present in the charge, their combination takes place in varying proportions.

The polymer product is then passed to a tower, where it is stabilized—after which it is fractionated into the *iso*octenes (dimers) and dodecenes (trimers). In general, the percentage of *iso*octenes in the polymer product is about 85 percent the balance being trimers. The polymer product produced is 30 percent of the butanes-butenes fraction charged to the unit. This is when producing *iso*octenes (85 octane) on the basis of a charge of 1:1 ratio of normal to *iso*butene. The *iso*octene fraction which boils between 200 and 260°F. is hydrogenated to *iso*octanes of 96 octane rating. The commercial unit described has a daily capacity of 1300 barrels of butane-butene fraction, producing therefrom 347 barrels of *iso*octenes and 43 barrels of trimers. The *iso*octenes are converted into *iso*octanes by catalytic hydrogenation.

TABLE 14
Catalytic Polymer Gasoline

Gravity, °API	67.9
ASTM Distillation, °F.:	
Initial boiling point	95
10-percent point	134
20-percent point	157
50-percent point	209
90-percent point	333
End point	430
Reid vapor pressure, lb.	8.3
Octane No. (CFR method)	81
Sulfur, percent	0.01
Gum (ASTM), mg.	12.3
Copper-dish gum, mg. per 100 cc.	81

TABLE 15
Composition of 100-Octane Fuel Containing 3 cc. Tetraethyl Lead Per Gallon

*ISO*pentane (Percent)	Aviation Gasoline (Percent)	*Iso*octane (Percent)	Reid Vapor Pressure (Lb. Per Sq. In. at 100° F.)
0	38.0	62.0	4.0
10	37.2	52.8	5.8
17	36.7	46.3	7.0
20	36.4	43.6	7.7
30	35.7	34.3	9.5
40	34.9	25.1	11.4
50	34.1	15.9	13.3

5. BLENDING OF *ISO*OCTANES

The *iso*octanes being produced commercially have a boiling range from 200-260°F. and, therefore, are not a complete motor fuel as to volatility. They require blending with hydrocarbons such as those of aviation-gasoline boiling range or *iso*pentane, or *iso*hexanes, in order to give volatility to the fuel. The blending values of 90, 95, and 100 *iso*octane fuels mixed with varying percentages of 65-, 70-, and 74-octane gasolines or *iso*pentane (90 octane) and then adding tetraethyl lead to produce a 100-octane fuel, are given in Figures 8, 9, and 10.

In some cases *iso*pentane is blended with *iso*octane

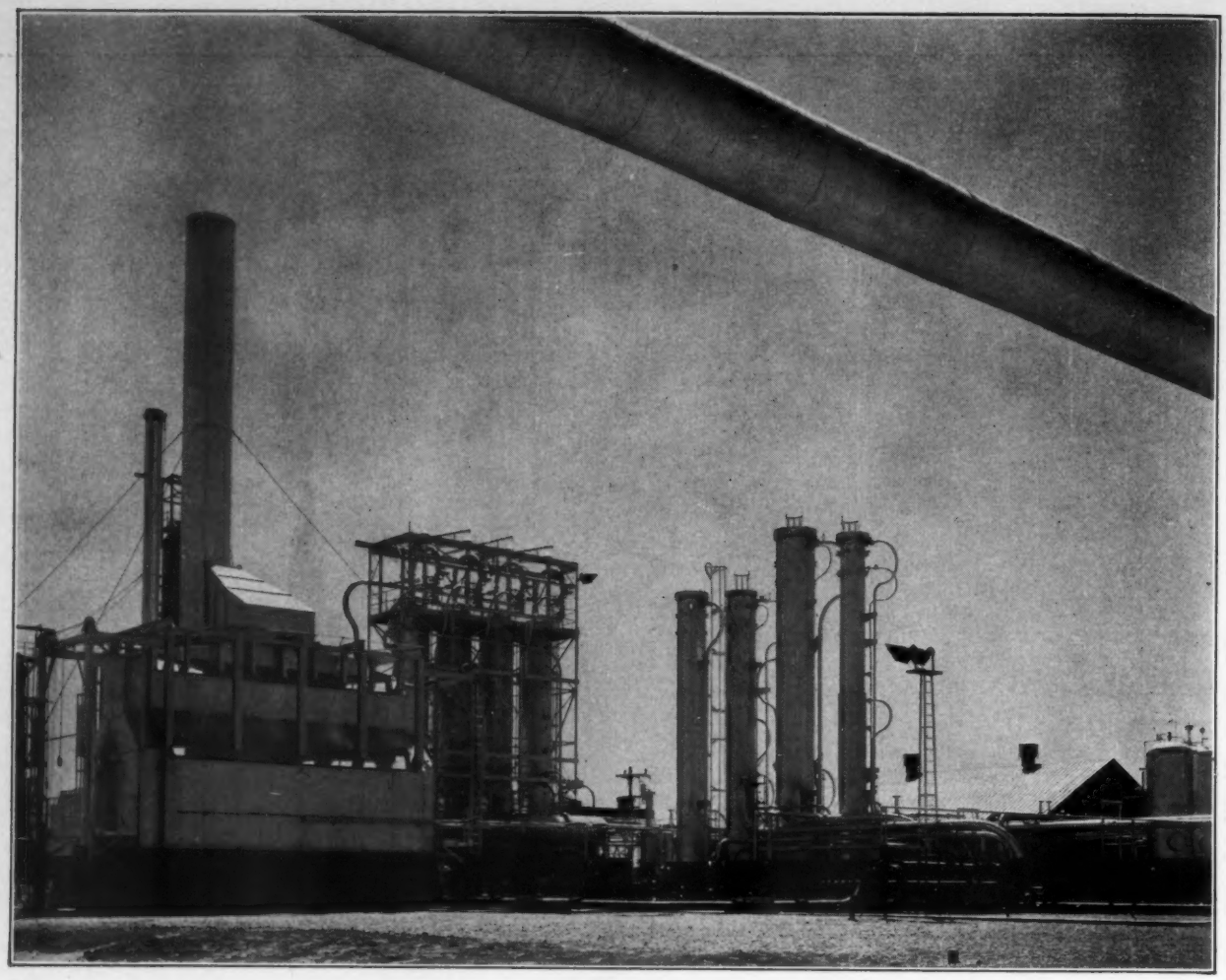

FIGURE 6
Butane-Cracking and Catalytic-Polymerization Unit (View 2).

and straight-run gasoline in order to provide the required front-end volatility to the *iso*octane. The volume of *iso*pentane is generally restricted to about 15 percent. The results of blending 100-*iso*octane fuel, 74-octane aviation straight-run of 7 pounds Reid vapor pressure, and *iso*pentane with 3 cc. of lead to produce 100-octane fuel are shown in Table 15.

The importance of *iso*octane in aviation fuel has been established for special uses such as military aviation and high-revenue transport. One may readily predict that within a short time all passenger planes will be operated with motor fuel of 100 octane or higher.

The dominant position of polymerization in the economy of motor fuel production is also definitely established in that small amounts of polymer gasoline may be used to correct an octane deficiency in the gasoline production of the refinery, and thus function to balance the quality of motor fuel produced.

SUMMARY

1. The polymerization process is one of the most important developments in the petroleum refining industry. More than 9,000,000,000 gallons of polymer gasoline may be produced yearly from the hydrocarbon gases in the United States, of which more than 1,000,000,000

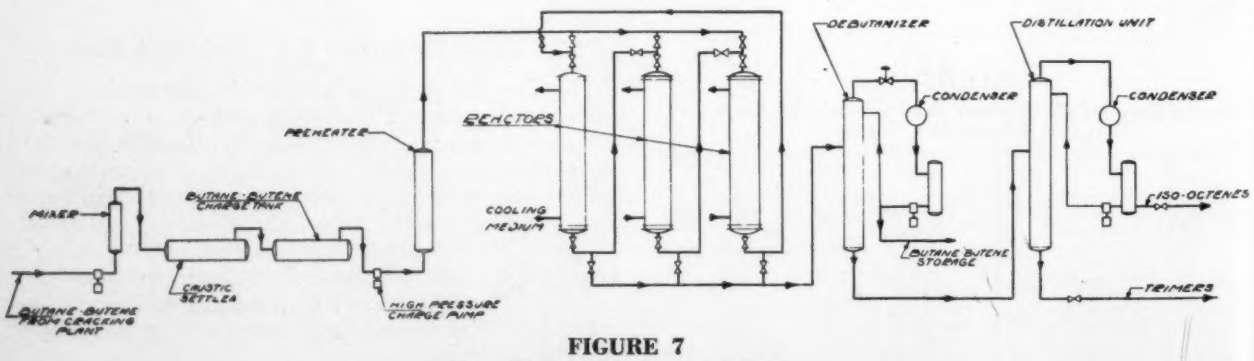

FIGURE 7
Flow Diagram, Isooctane Process.

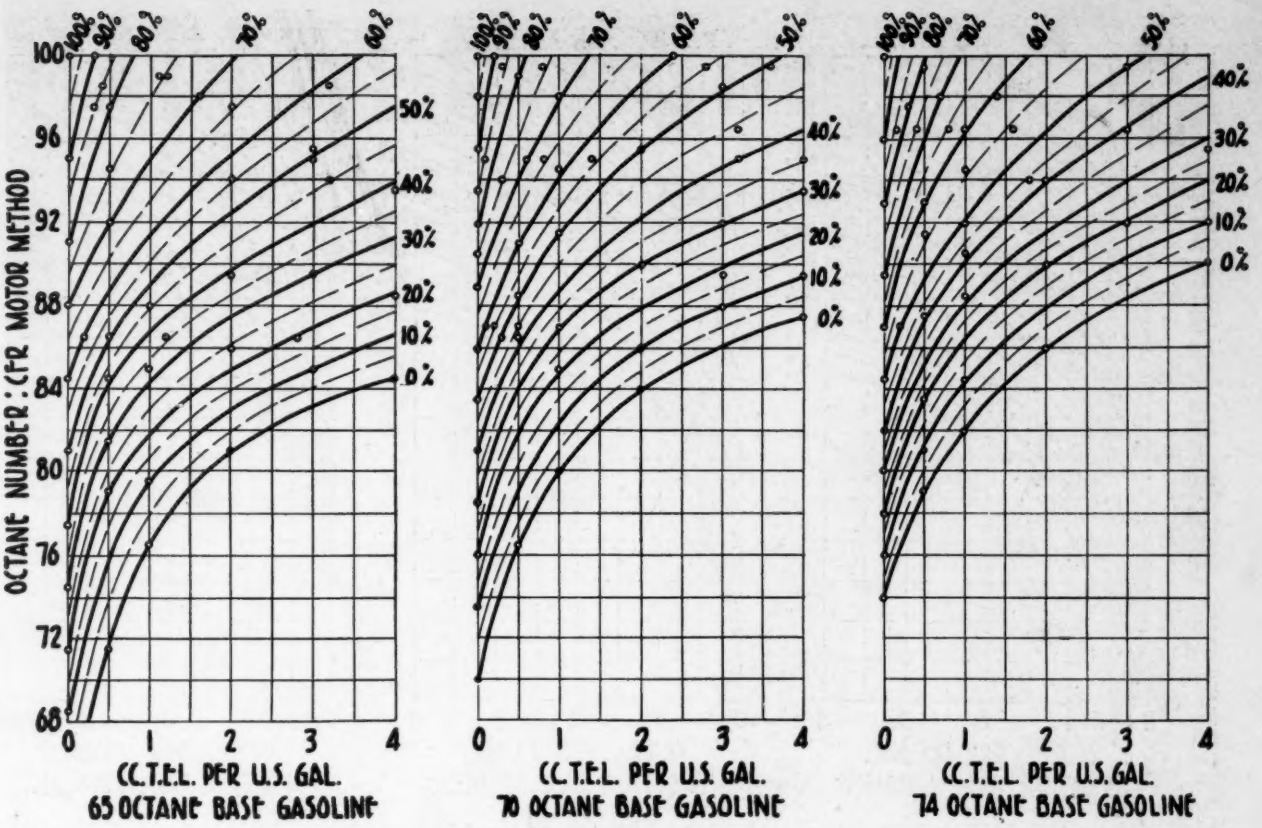

FIGURE 8

Blending Values of **Isooctane** *Fuels.*

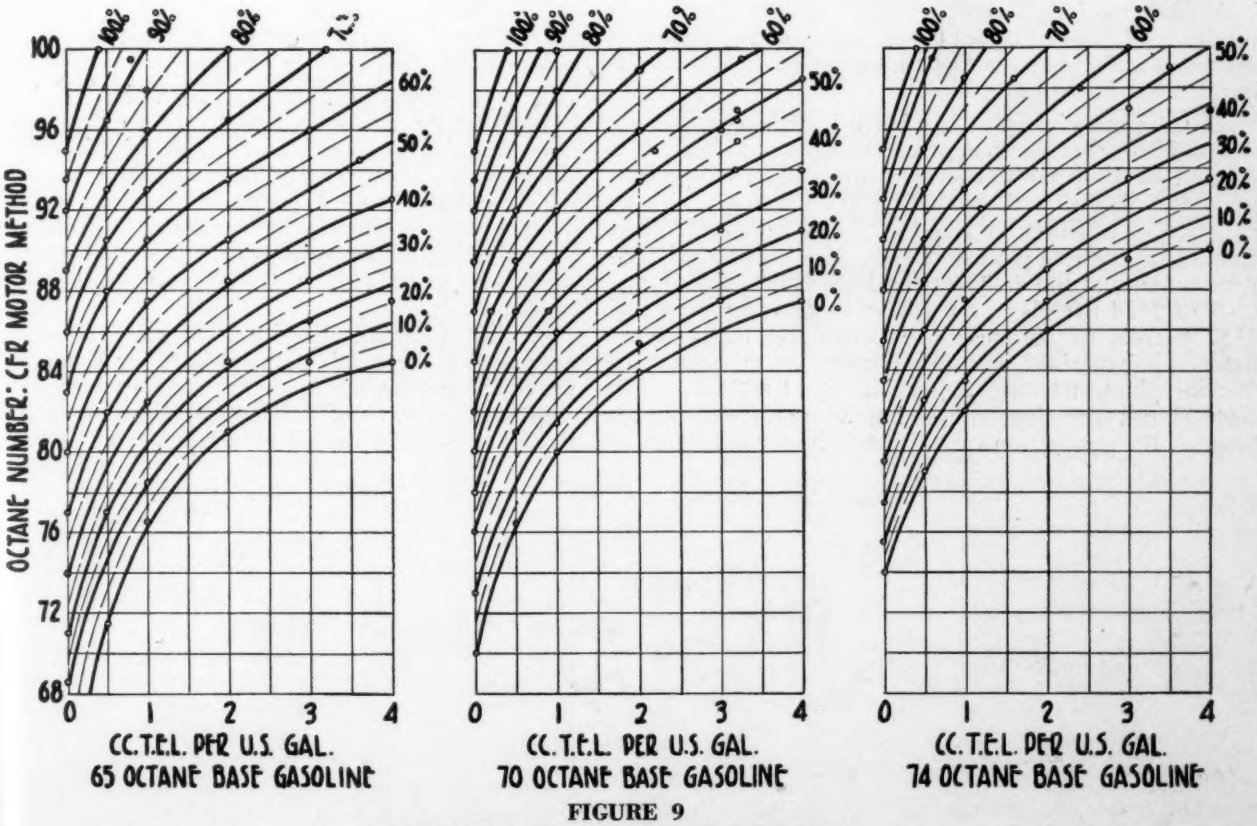

FIGURE 9

Blending Values of **Isooctane** *Fuels.*

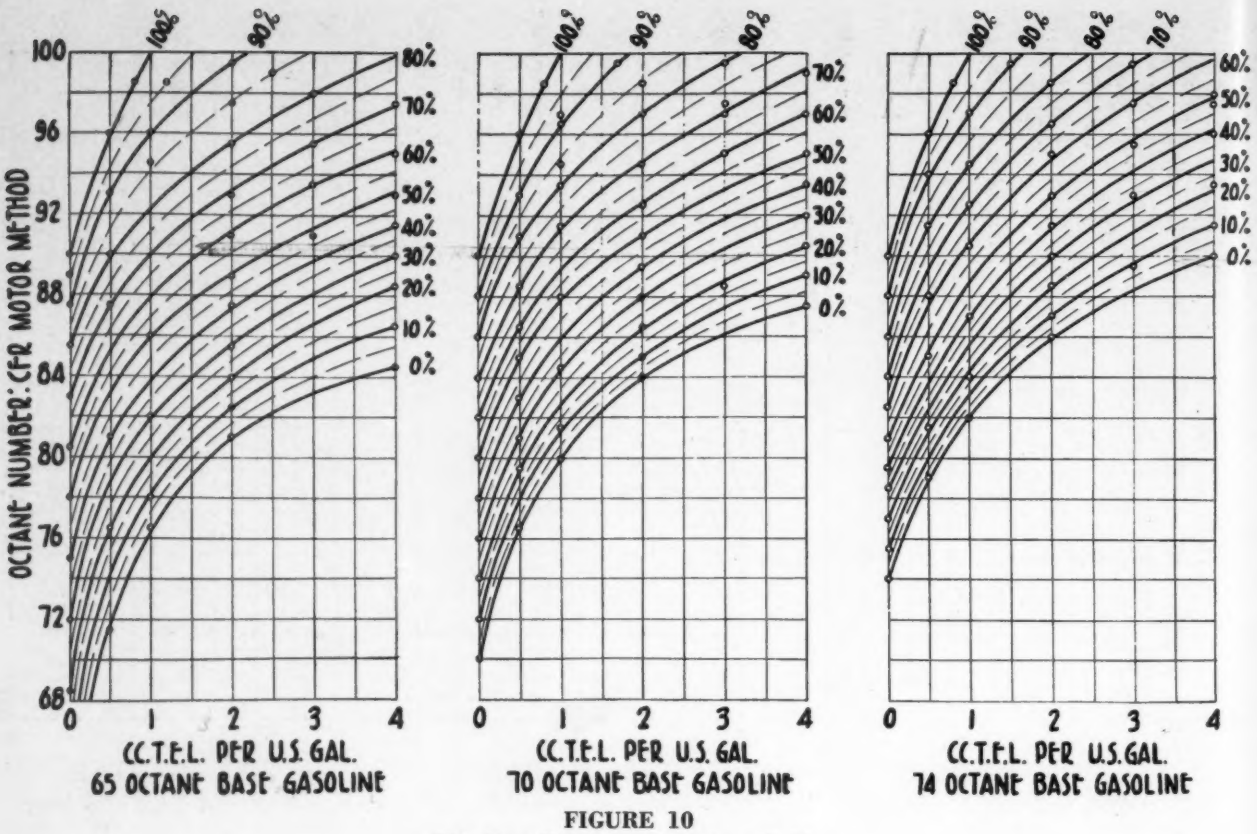

FIGURE 10

Blending Values of Isooctane Fuels.

gallons may be *iso*octane fuel of 95 to 100 octane rating.

2. Three modifications of the polymerization process have been described: *a*, polymerization of hydrocarbon gases containing propene and butene; *b*, pyrolytic cracking of butanes (and also propane) to produce olefin hydrocarbons followed by catalytic polymerization to produce polymer gasoline; *c*, selective polymerization of normal and *iso*butene and hydrogenation of the resulting octanes into *iso*octanes.

3. A commercial plant has been described processing daily 13,070,000 cubic feet of cracked gas containing 19.2 percent of propene-butenes, polymerizing 79.5 percent of these olefins, and producing 1080 barrels of true polymer in addition to 974 barrels of butanes. When treating a cracked gas containing 25.4 percent of propene-butenes at the daily rate of 13,874,000 cubic feet, a total of 1474 barrels of true polymer was produced and 1152 barrels of butanes. The percentage of propene-butenes polymerized was 86.5 percent. In another commercial plant, treating approximately 1,500,000 cubic feet of gas per day, containing 38 percent propene-butenes, the production was 250 barrels of polymer gasoline with a polymerization of 89 percent of the propene-butenes present.

4. A commercial plant, comprising a combination butane-cracking and catalytic-polymerization process, charges butane at the daily rate of 1090 barrels, producing 402 barrels of polymer gasoline made up of 109 barrels of pyrolytic polymer and 293 barrels of catalytic polymer gasoline.

5. A commercial plant has been described treating butane-butene mixtures selectively to polymerize the normal and *iso*butenes contained therein, having a daily capacity of 1300 barrels of butane-butene fraction, from which was produced 347 barrels of *iso*octenes. The *iso*octenes are catalytically hydrogenated to *iso*octanes, the latter having octane ratings of from 90 to about 100—dependent upon the conditions under which they are produced.

6. The economic position of the polymerization process for the production of polymer gasoline to improve the octane rating of the refinery output, or as a step in the process of making *iso*octanes, is now in relatively wide use in the oil industry.

Fuel Oil Production And Use

Present Status and Future Outlook For the Supply of Domestic and Industrial Fuel Oils in the United States

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THE market for domestic fuel oil has hardly been furrowed. Since 1930 the demand for domestic fuel oils has increased eight times as fast as the demand for gasoline. In this same period the number of oil burners installed increased 103 percent, and it has been shown how this very rapid installation of oil burners in the past few years has changed the refiners' production schedule; and, further, that an adequate supply of fuel oil has been, and will be, available to the consuming public at a reasonable price. There is, however, one definite way in which the oil-burner industry and the fuel-oil distributors can assist the refiners in producing this adequate supply of fuel oil at a fair price. This assistance to the refiner should be in the form of an earnest endeavor by these interested parties to reduce the number of grades of fuel oils now demanded for tank-wagon deliveries. It is well known that we are operating in this country more than 28,000,000 automobiles of numerous makes and models on two primary grades of gasoline. It should be possible to operate all of the 350 or more different makes and models of domestic oil burners on two primary grades of domestic fuel oil. The commercial burners operating automatically and without pre-heaters should be supplied with a grade to meet this service, and still another grade of heavier fuel should be available for industrial use. With this reduction in the number of grades of fuel oil to a total of four, the refiners can use their full efforts in producing quality fuel oils in volumes sufficient to meet the increasing demands.

It is well recognized that fuel oil must be inexpensive enough to stimulate the sale of oil burners, and must be generally available; and, finally, there must be a sufficient demand for standardized products to interest the petroleum industry in its production and distribution. The petroleum industry fully realizes the importance of producing fuel oils for this rapidly-expanding market, and has been rewarded for this service by an increase in the number of satisfied customers and an unprecedented increase in sales volume.

Finally, when we consider the magnificent technical improvements made in late years in the production, refining, and utilization of fuel oils and their adaptation to the services of mankind, we can look into the future with complete trust in the continued development of this important part of the petroleum industry.

This paper was presented at Eighteenth Annual Meeting, American Petroleum Institute, Chicago, November 11, 1937.

INTRODUCTION

IN order to understand the present position that fuel oil holds in the petroleum industry, a chronological review will show some of the reasons for its increasing importance. From the time petroleum was produced from the Drake well at Oil Creek, Pennsylvania, on August 27, 1859, and up to about 1910, kerosine was of prime importance to the refiner; then gasoline took its place. Men were deeply concerned over the probable failure of supplies of lamp oil required to meet the increasing demands, and were searching vigorously for a suitable substitute for sperm-whale oil which supplied the prime illuminating oils until the early 60's. The Drake well itself, 69½ feet deep and with an initial production of some 25 barrels daily, was important only because of the train of consequences which it set in motion. It was soon learned that petroleum was a raw material which was used to manufacture lamp and lubricating oils, and the industry continued on that basis until just after the beginning of the present century. After the turn of the century, large production of petroleum rising out of developments in Texas, Oklahoma, Kansas, and California, and the discovery of oil in Mexico, resulted in heavy fuels forcing their way into the fuel markets in competition with coal. With the general introduction of the internal-combustion engine about 1900, the industry entered a new cycle of production and consumption. The initial demand for both gasoline and fuel oil occurred about the same time.

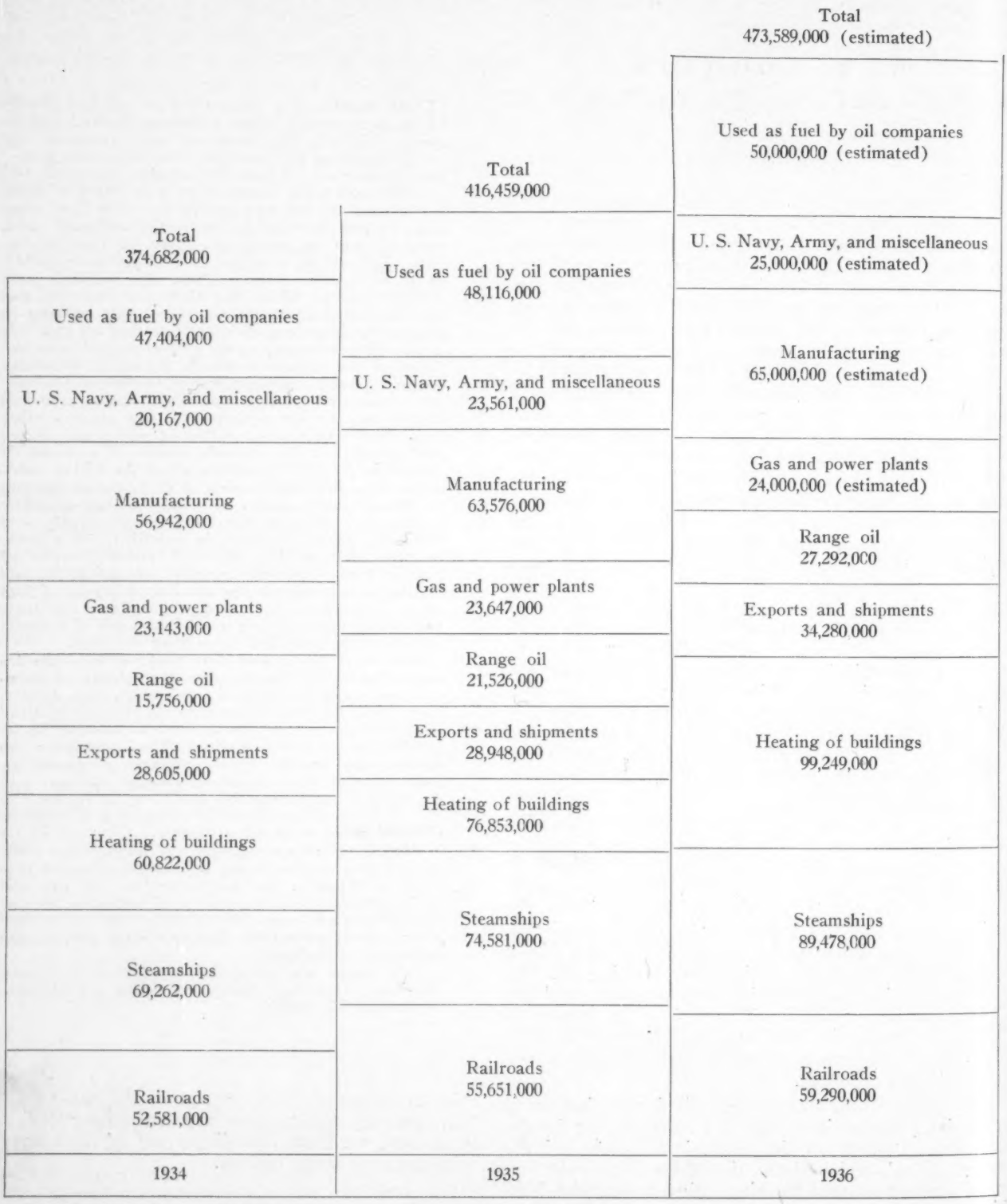
It is reported that oil burners were first used in the Russian oil fields, and later were installed on Russian steamships. When these ships docked at San Francisco, the fuel-oil-burning idea was approved and adopted by American manufacturers about 1900. The first reported installations were made on ships and in bakeries on the Pacific Coast. Fuel oil burners were rapidly replacing coal burners for ships, so that by the close of the World War virtually all of the navies were burning oil. The merchant marine followed the navy example, and the oil fuel tonnage of the world rose from 18 percent in 1920 to 40 percent in 1930, and to 50 percent in 1936. Today, about 40 percent of the oil fuel tonnage consists of Diesel powered ships.

This change from coal to fuel oils for marine use is still taking place, as is evident in a recent report for the fiscal year 1937 from the Statistical Bureau of the Panama Canal, which shows that there were only 977, or 18 percent of coal burning ships among the 5387 ships transitting the canal during the year. They further report that the number of motor ships (Diesels) is increasing, with a total of 2115 in 1937—although oil burners with 2236 ships are still in the majority. Motor ships represented 39.26 percent of the canal traffic in 1937, the only class to show an increase over 1936. From these data, we learn that 82 percent of the trans-canal ships are now using fuel oil.

RAPID CHANGE TO FUEL OIL

The use of fuel oil has spread to various industries since 1920, especially those with operations requiring

flexibility of heating, accurate temperature control, limited storage facilities, ease in handling, and freedom from ash, viz., such as manufacturing, railroads, office buildings, etc. The change in distribution of fuel oil consumption since 1934 is shown in Figure 1, "Gas-Oil and Fuel-Oil Deliveries by Uses, 1934-1936." In 1935, for the first time, the fuel consumed for heating buildings was 21 percent of the total and exceeded the amount used by steamships, which was 20.4 percent. This consumption for heating buildings continued to increase in 1936, so that it constitutes by far the greatest use in any single industry; it totaled 99,249,000 barrels, compared to 76,853,000 barrels in 1935, or a gain of 29 percent. Range-fuel sales, not included in the heating fuel total, showed increased volume in 1936, when deliveries reported to the U. S. Bureau of Mines totaled 27,292,000 barrels, or a 27-percent gain over the 1935 demand. The combined sale of heating and range oils, because range fuels are now used largely for heating, increased from about 25,000,000 barrels in 1926 to 126,-



Source: U. S. Bureau of Mines. (Figures in Barrels)

FIGURE 1

Gas-Oil and Fuel-Oil Delivery by Uses, 1934-1936.

541,000 barrels in 1936. It should be noted that the consumption has not materially increased in industries using heavy fuel oil in an approximate coal-oil parity basis. The demand will continue to increase in industries where liquid fuels have definite operating advantages over coal.

TOTAL ENERGY USED—COAL, PETROLEUM, GAS, WATER

Figure 2 shows the percentages of total energy utilized in this country from 1918. The energy survey of the U. S. Bureau of Mines shows that coal's contribution to the country's energy sources declined from 77 percent in 1919 to 54 percent in 1934 and, conversely, the substitute energies increased from 23 percent in 1919 to 46 percent in 1934. While these figures show rather a startling change away from coal, the over-all change from coal is reduced considerably when we compare the fuels where their uses are actually interchangeable. The U. S. Bureau of Mines total energy from petroleum includes lubricants, wax, road oil, and gasoline; and certainly coal could not replace petroleum products in these particular uses.

A. T. Shurick[1] has pointed out that almost invariably the true purport of the data has been misinterpreted, and has created a wrong conception of our energy supplies. Concerning this misconception, he has made the following statement: "It is important to note that the figures for 'domestic oil' and 'natural gas,' as in earlier issues of these tables, represent the entire production of crude petroleum and gas. Most of this production does not come in direct competition with coal. Much of the supply of both oil and gas is used in regions of the country, such as California and parts of the Southwest, where coal is available only at unusually high cost because of heavy transport charges. Nearly half the natural gas is used in the field for drilling or operating oil and gas wells and pipe lines, or for the manufacture of carbon black. More than half the oil is used in the form of gasoline, kerosine, and lubricants, for which purpose coal cannot well compete except at much higher levels of price. Even these refined products involve a certain measure of indirect competition with coal; for the energy market of the country is becoming more fluid and competitive, and a demand that cannot be met by one source of supply tends to fall back on the others. The purpose of these tables (Figure 2) is to measure the total demand for energy."

Deducting this non-competitive consumption from the total oil production in the U. S. Bureau of Mines tabulation, this leaves but 38 percent directly competitive with coal in the form of fuel oil.

He further points out that the use of natural gas in the producing fields for power and carbon black, and for other industrial uses, reduces the amount of this commodity in actual competition with coal by more than 47 percent. Mr. Shurick further states that "considered from the strictly competitive standpoint, as previously outlined, the bureau's figure of 53.7 percent as coal's share in the potential energy production of the country becomes 75.1 percent when the actual energies used in providing the heat and driving power alone are considered, and the proportion contributed by the substitute energies must, conversely, be reduced from 46.3 percent to 24.9 percent." These figures show that coal still furnishes about 75 percent of the power; and on this basis fuel oils are far from having saturated the market.

COAL Vs. FUEL OIL

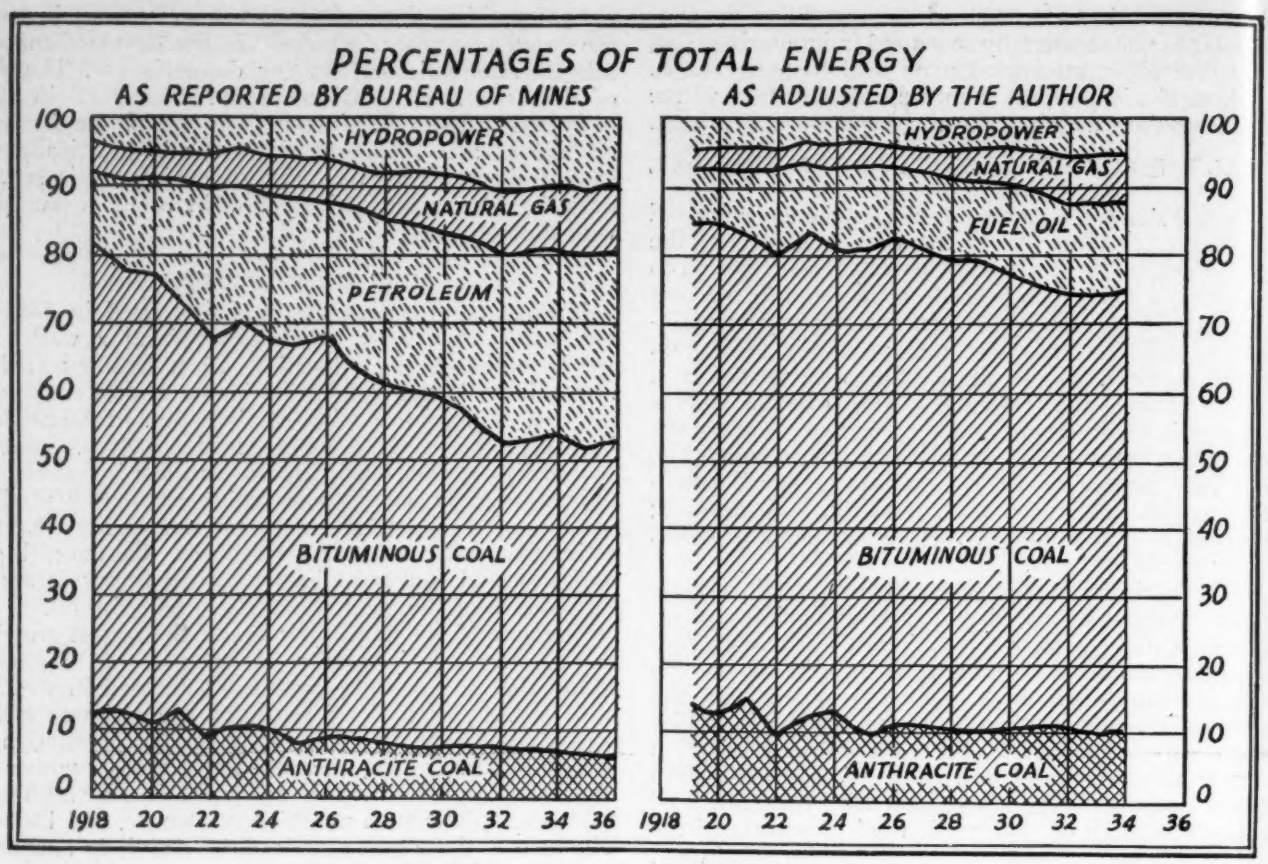
The coal industry, and especially anthracite producers, are making a strong bid for household heating through the introduction of residential stokers. In order to protect this household heating trade against fuel oil and gas competition, the coal producers are cooperating with the "appliance manufacturers" in the development and sale of automatic stokers for domestic use. The sale of domestic stokers has increased from 7000 in 1932 to 76,000 in 1936. The installation cost for the domestic oil burner and the domestic stoker is practically the same today, so that the price of coal for this service must be kept comparatively low in order to compete with domestic fuel oil.

GAS COMPETITION

History records that gas was first used in 1821 in Fredonia, New York, when piped from a well to a nearby building. Since that time it has become a fuel of major importance, and is distributed almost nationally through thousands of miles of pipe lines. In the producing fields, gas is used for generating power. Some is changed to carbon black for use as filler in automobile tires, and lately has become an important raw product for the production of a number of new chemicals. It is estimated that about 55 percent of the natural gas produced and consumed in the United States comes to the surface of the ground in association with oil.

The natural gas industry is one of the fastest growing natural resource industries. A reference to Figure 2 shows that the use has practically doubled in the last 10 years. Prior to 1925 much of the gas was either wasted or sold at a very low rate for the production of carbon black. During the past 10 years a number of pipe lines has been built from the Louisiana and Texas fields to markets such as Chicago, Denver, and Detroit. The cost of these pipe line facilities definitely limits the areas in which natural gas can compete with fuel oils, especially for domestic service. It is estimated that it costs about 2 cents per 100 miles, per thousand cubic feet, to transport natural gas to any particular "city gate." In addition to transportation cost, there must be added the cost of raw material at the well, plus the fixed charges of physical properties in the city necessary for distribution. In addition to these high costs of physical properties, another limiting factor in extending the number of gas customers and total consumption is based on the "peak" load of the gas distributing system, even though this peak is reached only for a matter of minutes in any season. This limiting factor of the peak load is not effective in fuel oil distribution. It is expected that the distribution of natural gas to domestic and commercial consumers will continue to expand and replace manufactured gas, because today it represents only about 56 percent of the volume of gas distributed for these uses.

The gas companies throughout the country are utilizing extensive advertising campaigns to obtain additional consumption of both commercial and domestic gas. While the advertising has probably resulted in the loss of some fuel oil accounts, it has definitely aided in selling automatic heat. During the past few years some gas companies have guaranteed heating costs over a season, and in many cases have found that their estimates were somewhat low. They have profited by this experience, and now make a complete engineering survey of the house, and they now require insulation, weather stripping, and other features before they will definitely guarantee the season heating cost. The oil industry can well follow the lead of the gas companies in advising the customer on building changes which would result in lower fuel oil consumption. Table 1 shows how it is possible to make fuel oil even more economical by the adoption of storm windows, insulation, and weather stripping. By the adoption of a combination of these insulation features, it is possible to save up



Net Changes in Percentages of Total Energy

	Total Production (U. S. Bureau of Mines)			Competitive Consumption (By A. T. Shurick)!		
	1919	1934	Decrease	1919	1934	Decrease
Anthracite	12.7	7.6	39	14	10.6	24
Bituminous	64.7	46.1	29	71	64.5	11
Total coal	77.4	53.7	31	85	75.1	12
			Increase			Increase
Oil	13.7	27.7	102	8	13.5	69
Natural Gas	4.2	9.3	121	3	6.6	120
Total oil andzgas	17.9	37.0	106	11	20.1	83
Hydropower	4.7	9.3	100	4	4.8	20
Total substitutes	22.6	46.3	105	15	24.9	66
Grand total	100.0	100.0	...	100	100.0	...

to 52 percent on fuel oil consumption. The effects of these various insulating materials should certainly be brought to the attention of fuel oil customers and prospects.

The prospective fuel oil consumer is usually interested in the comparative consumption of fuel oil, coal, and gas. Table 2 is a comparative estimate of the yearly fuel requirements and equivalents, and is calculated for average heat contents and average heating efficiencies. By using the local fuel prices, the prospect or customer can easily calculate his seasonal requirements and approximate cost by means of this table.

Table 3 shows an estimated comparison of fuel costs in the New York City area with the estimated costs of the various competitive fuels, based on an annual consumption of 10 tons of hand-fired nut coal. It must be realized that these figures cannot be taken as actual, and are only intended to show approximate comparative costs.

THE REFINER'S CHANGING HORIZON

In considering ways and means for meeting the fuel oil demand in the future, it is advisable to divide the subject into two distinct parts: 1, the demand for distillate fuels and, 2, the demand for heavy fuel oils or bunker "C" type fuels. It is recognized that considerable quantities of heavy fuel oils are consumed annually in under-boiler service for steam generation, and were originally in competition against coal on the coal-oil parity basis. In some of these cases, fuel oil does not possess any real advantages, and cannot be priced to include any increased return for the desirable properties of a liquid fuel. This coal-oil-parity market is becoming less and less attractive to the fuel oil producer, for in many cases heavy-fuel-oil production will be incidental "to the balancing of the gasoline and distillate-fuel-oil demands." This marginal demand for heavy fuel will probably not increase to any great extent unless the prices of coal are materially increased.

The balance of this paper will be devoted primarily to a discussion of distillate fuels.

The refiners and distributors of petroleum products have been forced by nature or circumstances of their own inventiveness to change their major production

TABLE 1
Required Installations for Household Heating

Storm Windows	½-In Insulation	Weather Stripping	Approximate Savings (Percent)
×	..	..	25–30
..	×	..	20–30
..	..	×	15–20
×	..	×	27–32
..	×	×	40
×	×	..	50
×	×	×	52

The "×" marks indicate various methods of reducing heating costs additionally by installation of storm windows, insulation, and weather stripping. These figures are based on a house not equipped with any of these devices.

TABLE 2

Yearly Fuel Requirements and Equivalents*

Tons of Coal or Coke	Tons of Stoker Coal	Gallons of No. 3 Oil	Therms of Gas	Thousands of Cubic Ft of Manufactured Gas	Thousands of Cubic Ft of Natural Gas	Thousands of Cubic Ft. of Mixed Gas
5	4.2	685	924	168	92	115
6	5.0	822	1,108	202	111	138
7	5.8	959	1,293	235	129	162
8	6.7	1,096	1,478	269	148	185
9	7.5	1,233	1,663	302	166	208
10	8.3	1,370	1,847	336	185	231
11	9.2	1,507	2,032	370	203	254
12	10.0	1,644	2,216	403	222	277
13	10.8	1,781	2,401	437	240	300
14	11.7	1,918	2,586	470	259	323
15	12.5	2,055	2,771	504	277	346
16	13.3	2,192	2,955	538	296	369
17	14.2	2,329	3,140	571	314	392
18	15.0	2,466	3,325	605	333	415
19	15.8	2,603	3,509	638	351	439
20	16.7	2,740	3,694	672	369	462
21	17.5	2,877	3,879	706	388	485
22	18.3	3,014	4,063	738	406	508
23	19.2	3,151	4,248	773	425	531
24	20.0	3,288	4,433	806	443	554
25	20.8	3,425	4,618	840	462	577
30	25.0	4,110	5,542	1,007	554	693
35	29.1	4,795	6,465	1,175	647	808
40	33.3	5,480	7,389	1,345	739	924
45	37.5	6,165	8,312	1,511	831	1,040
50	41.6	6,850	9,236	1,679	924	1,155

**The Oil-Burner Owners Savings Book*, published by Shell Union Oil Corporation (1937).

product. There was a time when refiners boasted that they were producing almost one half a barrel of kerosine from each barrel of crude refined. The remarkable changes in yields of various products is apparent in Table 4, which shows the principal products from crude oil from 1914 to 1936. During this 20-year period the average yield of gasoline has been increased from 18.2 to 44.1 percent, while the yield of kerosine has decreased from 24.1 to 6 percent. During this same period there has been both an increase and decrease in the yield of gas oil and fuel oil, showing a decrease from 46.5 percent in 1914 to 38.5 percent in 1936—although for individual years there were considerable fluctuations.

The crudes of different producing oil fields contain a very wide variation in the percentages of the petroleum products into which they can be separated. The modern refiner may run many different grades of crude oil—not merely because these several grades are particularly economically available to that refinery, but because certain of the grades contribute a desirable yield of products or a required specification of product. A refinery on the Eastern Seaboard may operate on crudes from several foreign countries as well as on crudes from Texas, Gulf states, and Pennsylvania. One grade of crude may contain a major percentage of gasoline which may be either good in anti-knock grade (high octane) or bad in anti-knock (low octane), a high percentage of Diesel fuel of high or low-octane number, or a high percentage of kerosine which may be either good or poor in burning quality. The next yield may be lubricating oil or, instead of a lubricating oil, the final product may be fuel oil or asphalt. The percentage of gas oil obtainable from crude may vary from a trace in heavy Mexican crude up to 52 percent in a Mirando crude. A Mid-Continent crude would yield about 30 percent; a Smackover, 40 percent; a California (25° A.P.I.) 15 percent; and a Colombia, South America (31° A.P.I.) 27 percent.

At the present time there are several other changes taking place in the composite refinery picture, because the domestic oil burner has created an additional demand for distillate fuel oils. The influence of increased demand for distillate fuels does not show in Table 4, because both heavy and light fuels are grouped together. This has been changed, as brought out in a recent statement from the U. S. Bureau of Mines:[2] "The consensus of opinion indicated that the marketing grades 1 to 4, usually designated the heating oil, coming within the gas-oil-distillate-fuel-oil range and that grades 5 and 6 covered the heavy or residual fuel oils. Consequently, the oil companies were requested to report their heating-oil sales under these two general headings. A tabulation of the incoming statements shows that light or distillate fuel oils designated by grades 1 to 4 for the purpose of this survey totaled 69,429,000 barrels, or 69.9 percent of the 1936 heating-oil sales, and that grades 5 and 6 were used for heating to the extent of 29 820,000 barrels, or 30.1 percent of the total demand. This recently-developed demand has forced the refiners to classify distillate fuel oils in the principal-product classification, to share this distinction with gasoline; and places a direct and definite responsibility on the American petroleum industry to meet these growing requirements in the same satisfactory manner in which they have met the increasing motor fuel demand."

Comparing the yield of distillate fuel oil as given in Table 5 for the year 1934 with yield for the year 1936, the total yearly increase has been from an average of 10.60 percent in 1934 to 11.76 percent two years later. The total fuel oil yield, including kerosine. for 1936 was 43.76 percent compared with a yield of 44.13 percent for motor fuel or gasoline.

Figure 3 shows proportion of crude oil converted into gasoline and fuel oil, 1918 to 1936. This shows that

TABLE 3

Estimated Comparison of Fuel Costs—New York City Area

Legend	Nut Coal Hand-fired	Nut Coal, Stoker-fired	No. 1 Buck, Blower—Hand-fired	No. 1 Buck, Stoker-fired	Rice, Stoker-fired	Soft Coal, Stoker-fired	Coke, Hand-fired	Oil Conversion Job	Oil-Burner Unit	Gas Conversion Job	Gas-Boiler Unit
Cost per unit	$10.50 *a* per ton	$10.50 *a* per ton	$7.35 *a* per ton	$7.35 *a* per ton	$6.50 *a* per ton	$7.10 *a* per ton	$11.25 *a* per ton	$.075 *b* per gal.	$.075 *b* per gal.	$.55 (per M. C. F.*	$.55 (per M. C. F.*
Heat value of fuel as fired (potential B. t. u.)	12,500 per lb.	12,500 per lb.	12,000 per lb.	12,000 per lb.	11,500 per lb.	14,000 per lb.	13,000 per lb.	138,000 per gal.	138,000 per gal.	550 per cu. ft.	550 per cu. ft.
Average efficiency	50%	65%	50%	60%	60%	60%	50%	60%	70%	60%	75%
Effective heat value (B. t. u.)	6,250	8,125	6,000	7,200	6,900	8,400	6,500	82,800	96,600	330	413
Useful heat obtained for 1 cent	11,905	15,476	16,327	19,592	21,231	23,662	11,556	11,040	12,880	6,000	7,509
Comparative cost per unit of heat per million B. t. u.	100% $.840	77% $.646	73% $.612	61% $.510	56% $.471	50% $.423	103% $.865	108% $.906	92% $.776	198% $1.66	158% $1.33
Cost of fuel per season based on 10-ton hand-fired furnace	$105.00	$80.85	$76.65	$64.05	$58.80	$52.50	$108.15	$113.40	$96.60	$207.90	$165.90
Annual consumption	10 tons	7.7 tons	10.4 tons	8.7 tons	9 tons	7.4 tons	9.6 tons	1,500 gal.	1,300 gal.	378,000 cu. ft.	302,000 cu. ft.

*Thousand cubic feet.
a Burns Bros., 9–30–37.
b Shell Union Oil Corp., 9–30–37.
c Consolidated Edison Co. of New York (average) 10–1–37.

TABLE 4
Principal Products from Crude Oil[3]

Year	Gasoline and Naphtha (Percent)	Kerosene (Percent)	Gas Oil and Fuel Oil (Percent)	Lubricants (Percent)
1914	18.2	24.1	46.5	6.6
1918	25.3	13.3	53.5	6.2
1920	26.1	12.7	48.6	5.7
1922	28.8	11.0	50.9	4.7
1924	31.2	9.3	49.8	4.3
1926	34.9	7.9	46.9	4.1
1928	37.4	6.6	46.7	3.8
1930	42.0	5.3	40.2	3.7
1932	44.7	5.3	35.9	2.7
1934	43.4	6.0	37.5	2.9
1935	44.3*	5.7	37.2	2.9
1936	44.1*	5.2	38.5	2.9

*Gasoline only.

TABLE 5
Average Yields—Motor Fuel and Fuel Oils*

Year:	1936 (Per Cent)	1935 (Per Cent)	1934 (Per Cent)
Kerosine	5.25	5.78	6.01
Distillate fuel oil plus gas oil	11.76	10.38	10.60
Residual fuel oil	26.75	26.90	26.84
Total yield, fuel	38.51	37.28	37.44
Total yield, fuel and kerosine	43.76	43.06	43.45
Motor fuel	44.13	44.30	43.09

*U. S. Bureau of Mines.

the gasoline yield equaled and crossed the fuel oil yield early in 1931. It further shows that the fuel oil yields are increasing, so they may again equal gasoline at an early date.

In order to maintain a satisfactory, fuel-oil-gasoline supply-demand relationship, it will be necessary: 1, that the winter demand for gasoline continue to increase; 2, that, in the process of meeting the seasonal demand for fuel oil, excess of gasoline is not produced.

In order to make a material increase in the yield of distillate fuels, it may be necessary to sacrifice gasoline production and to crack heavy fuel oils to produce additional yields of distillate fuel oils and a residual product of solid coke. This method sacrifices yield of heavy fuels for the production of additional volumes of distillate fuels. The necessity for the adjustment of refinery methods was brought out during the cold weather in 1935-36 season, at which time the refiners not only found it necessary to increase their yield of distillate fuels per barrel of crude run to stills; but, to meet this emergency, it was necessary to run more crude to stills than was actually needed to produce the required gasoline, and this resulted in a surplus of gasoline in the Mid-Continent at an unseasonable time. The yield of distillate fuels in the United States refineries varied from 8.47 percent in 1932, when prices were on a decline, to a peak of 13.65 percent in February 1936 (Figure 4).[4] The East Coast refiners changed their runs to get an even greater yield, and in February, 1936, produced 14.24 percent of distillate fuel from each barrel of crude run to stills. Yield, then, is definitely affected by seasonal demand as well as by price. In order to bring out this comparison, Figure 4 also shows the tank car price of No. 2 fuel oil at New York in cents per gallon.

If in refinery operations it is necessary to sacrifice gasoline yield to increase distillate fuel yield, then the increased demand for distillate fuels can be met: first, by increasing the total crude oil charged to stills to take care of motor fuel demands and, second, by getting a refinery price for the distillate which will make it economical to produce larger volumes of such a product. The price of distillate fuel at the refinery approaches the price of gasoline, and has been in that position for some years, as indicated by the following prices: "The average tank car price for No. 2 fuel oil, New York harbor, January 30, 1930, to December 31, 1936, was 4.64 cents per gallon; while the average tank car price of gasoline was 6.27 cents per gallon during the same period. The differential between the two products for seven years has thus been only 1.63 cents per gallon."[4] It is of further interest to note that the average retail price of No. 2 fuel in New York for the past seven years has been 6.85 cents per gallon, and the average price during this last heating season was down 24 percent from 1926.

Now that domestic fuels have attained a major product classification in refinery operation, it is necessary for them to share a part of the cost of the raw material and contribute a greater portion of the total income of the industry. Considered in another way, a barrel of crude will allow only a certain total number of gallons of finished product, and the increase in yield of gasoline or of distillate fuels is at the expense of the other; so that the refiner's problem today is to produce more distillate fuel and comparatively less gasoline. Some of the recent developments in the science of refining that assist with this problem are reforming, polymerization, viscosity-breaking, and non-residuum cracking. In the non-residuum cracking the final product is a solid coke, rather than a liquid fuel (bunker or No. 6), and this operation yields a greater percentage of distillate products.

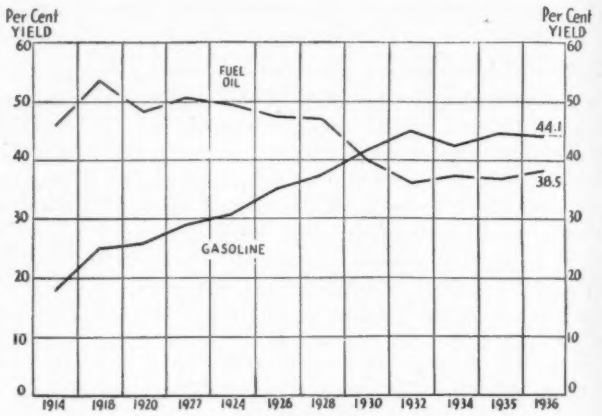


FIGURE 3
Percent Yields of Gasoline and Fuel Oil from Crude Oil 1914-1936.

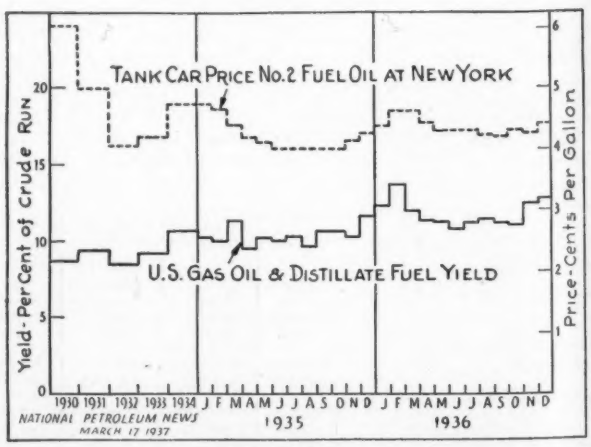


FIGURE 4

The past three-years' trend indicates that by 1940 the demand for distillate fuels, including range fuel, for domestic use will approximate 14,000,000 barrels. The 1936 sales of 96,000,000 barrels are estimated to

TABLE 6
Domestic Demand for Petroleum Products in 1936 as Compared with 1935

(From U. S. Bureau of Mines Report)
(Figures in Barrels)

Product	1936	1935	Percent Change
Motor fuel	481,591,000	434,810,000	+11
Kerosine	51,479,000	47,645,000	+8
Gas oil and fuel oil	408,991,000	366,723,000	+12
Lubricants	22,676,000	19,661,000	+15
Wax	1,076,000	933,000	+15
Coke	6,267,000	6,703,000	−6
Asphalt	22,185,000	15,652,000	+41
Road oil	7,689,000	5,962,000	+28
Still gas	54,441,000	51,184,000	+6
Miscellaneous	2,223,000	1,973,000	+12
Losses	34,545,000	32,440,000	+6
Total domestic demand	1,093,163,000	983,686,000	+11
Daily average	2,987,000	2,695,000	+11

increase as follows: 1937, 105,000,000 barrels; 1938, 117,000,000 barrels; 1939, 128,000,000 barrels; 1940, 140,000,000 barrels. It is also expected that the gasoline consumption will increase about 20 percent during the same period.

The U. S. Bureau of Mines reports for the past two years show the demand of the various products and percentage change for the United States from all crudes, as set out in Table 6. It will be noted in Table 6 that the 1936 demand for gas oil, fuel oil, and kerosine totaled 460,700,000 barrels, or approximately the same as motor fuel which was 481,591,000 barrels.

The demand for domestic heating oils, distillate fuels, and gas oils from 1934 through 1936 increased an average of 17 percent per year.

The consumption of fuel oil for heating was 99,249,000 barrels.* The total gas-oil, range-fuel, and distillate-fuel demand for 1936 was 126,541,000 barrels; during the same period the gasoline demand was 481,591,000 barrels, or a ratio of approximately 1 barrel of domestic fuel oil to 4 barrels of motor fuel. This trend of increase in both commodities will probably change during the next few years. The demand for motor fuel will level out, and the demand for distillate fuels will increase. This increase, of course, will depend on the sale of new oil burners. The annual demand for domestic fuel oil and kerosine (range fuel) is 126,000,000 barrels—which leads us to believe that the industry has progressed into another definite stage of its development. Just as refiners have been forced to adjust their kerosine yields to obtain more gasoline, so in the future it will be necessary for the refiners to adjust their gasoline and heavy-oil yields to produce more distillate fuels.

In order to meet this increasing demand for the various petroleum products, which averaged 11 percent last year, it has been necessary continually to increase the allowable crude production in the various producing states along with corresponding increase in volume of crude run to the refining stills. The crude-oil production has increased almost continuously from some 2,000,000 barrels daily in 1931 to the all-time high record of 3,745,500 barrels daily in the week of August 28 of this year. The run of crude oil to stills has increased along with crude production, so that the daily throughput is about 3,500,000 barrels.

PRODUCING DISTILLATE FUELS

The modern method of refining crudes involves two major processes: *a*, crude oil is distilled or topped, yielding gasoline, kerosine, and other products such as gas oil, and a fuel-oil residue; and *b*, the residue or gas oil from (*a*) may subsequently be cracked to produce gasoline, cycle stock (cracked gas oil), and a cracked fuel-oil residuum. The gas oil and straight-run fuel-oil residue from (*a*) may be cracked by one of the following methods:

1. Cracked to liquid residuum.
2. Non-residuum operation, i.e., cracked to solid residue of coke.

The method of operating the cracking may again be divided into several classifications, depending on liquid-phase or vapor-phase operation, high-pressure or low-pressure operation, limited cracking to break viscosity, etc.

By using method (1) there is produced about 41 percent gasoline, 12 percent cycle stock or gas oil, and 36 percent residuum fuel oil. By utilizing method (2) or non-residuum, the gasoline is increased to 49 percent, cycle stock or gas oil to 14 percent, and the fuel oil is reduced to 7 percent with a yield of about 70 pounds of coke per barrel input charged to unit. The method selected for operation depends on several factors, viz., gasoline prices, coke prices, fuel-oil prices, type of cracking unit used, etc. The non-residuum operation produces a greater yield of gasoline, an additional yield of gas oil suitable for fuel-oil distillate, much less heavy fuel, and a greater yield of gas which can now be utilized by the polymerization process to produce a high-octane gasoline.

Coke now finds a ready market by being mixed with coal in about equal proportions and sold for domestic fuel. In most cases it is not economical to use reduced or uncracked crude for heavy fuels. It should be cracked to produce gasoline and fuel-oil distillates, which distillates can be treated to produce domestic grades of fuels.

Petroleum coke now finds a ready market as such or, after having been mixed with coal in about equal proportions, it is sold for domestic fuel. In most cases it is not economical to use reduced or uncracked crude for heavy fuels. It should be cracked to produce gasoline and fuel-oil distillates, which distillates can be treated to produce domestic grades of fuels.

DISTILLATE FUEL-OIL DEMAND

A comparison between the demand for motor fuel and fuel oils forcibly demonstrates that fuel oil must be considered not as a by-product, but as a co-product with motor fuel. Since 1930 the number of motor vehicles in the United States has increased 7 percent, and the domestic demand for motor fuel has increased 22 percent. In this same period the number of domestic oil burners installed in the United States increased 103 percent, and the consumption of fuel oils has increased 113 percent. *A comparison of consumption figures shows that the domestic heating-oil demand has increased eight times as fast as the gasoline demand.*

Each domestic oil burner is of far greater importance to the oil industry in the matter of total petroleum products consumed than is each motor car. A motor car consumes an average of 700 gallons of gasoline, while the average oil burner consumes 48 barrels, or approximately 2000 gallons of fuel oil. On this basis, each domestic oil burner uses about three times as many gallons of petroleum as each motor vehicle each year.

This increase in gasoline demand and the very rapid increase in distillate-fuel-oil demand have forced the refiner to change his traditional plan of operation. Crude oil runs to stills are now maintained at a fairly stable rate throughout the winter in order to keep the nation's homes supplied with domestic fuel oil. Even though the refiner runs his crude to obtain a higher yield of fuel oil

*U. S. Bureau of Mines report.

and gas oil than usual, and reduces the gasoline yield, fuel-oil demand has resulted in adding more gasoline to storage during January, February, and March than in the past. This makes it important that the refiner recognize changing demands so that gasoline production and consumption will remain in balance throughout the year. Such changes in consumption of petroleum crudes require a number of adjustments in refiners' processes. These adjustments are technically possible; but, in the last analysis, are controlled by the price ratio between the different products produced. A reference to Figure 5 shows a somewhat different average yield from year to year; it likewise shows the seasonal production of distillate fuel oils in both the Gulf and East Coast refineries, also an average for the country. The definite peak on increased yields during the winter months for distillate fuels demonstrates that the refiners are able to change their operations to produce the product most in demand.

DIESEL-FUEL DEMAND

The high-speed Diesel engine is a large consumer of distillate fuels; for from 1932 to 1936 the annual sale of Diesel horsepower increased from 130,000 to 1,830,000. It is further estimated that about 90 percent of the Diesel engines sold in 1936 were less than 100 horsepower. This change to Diesel engines of lower horsepower has affected domestic fuel oil in two ways:

1. Diesel engines of lower horsepower and higher speeds require a fuel of lower viscosity and lower boiling point similar to that required for domestic oil burners. These smaller Diesel engines will probably operate 3000 hours per year, and would have an annual consumption of perhaps 4½ barrels per horsepower-hour per year. On this basis, a 60-horsepower Diesel engine would consume 270 barrels of fuel per year, or approximately five times the average consumption of a domestic oil burner.

The new installations of low-horsepower Diesel engines in 1936 required an additional volume of approximately 7,500,000 barrels of distillate fuel.

2. In many cases the smaller engines are not equipped with sufficient storage capacities to take barge or tank car deliveries, so they are supplied mainly through tank wagon deliveries. This newly-created consumption tends to place an additional delivery load on the fuel-oil distributor, but at the same time will tend to equalize his deliveries because the consumption will usually cover a full 12-months' period.

LOCATION OF OIL-BURNER MARKET

The burner markets are changing their geographic location, especially since 1929. Table 7 demonstrates the extent of this change.

Table 7 shows that 18.3 percent of the sales have moved from the Pacific and Middle West to the Atlantic seaboard. Today, the prime domestic-burner market includes New England, Middle Atlantic states (except western Pennsylvania), the Middle West (except Ohio), and Washington and Oregon. These sections represent from 82 to 85 percent of yearly domestic burner sales. Permits for burner installations issued for this year indicate that the trend of increased sales is still along the Atlantic seaboard. If this same trend holds over the next four years, which shows 80 percent of the burners being sold in this area, then there will be a demand for an additional volume of approximately 50,000,000 barrels of distillate fuel per year for distribution along the Atlantic seaboard, north of Richmond, Virginia, and east of Rochester, New York.

TABLE 7

Geographic Distribution of Oil-Burner Sales

	1929 (Percent)	1936 (Percent)
Pacific Coast	9.2	4.1
Middle West	27.4	14.2
Middle and South Atlantic	19.3	30.0
Metropolitan New York	26.4	31.5
New England	17.7	20.2

The sale of domestic burners has been further accelerated by the rapid decrease in average retail prices since 1929. The *Fuel Oil Journal* reports that the average price for a conversion burner installed in 1929 was $692, while this price was gradually decreased until the average price in 1936 was only $304, and a complete boiler burner unit could be purchased and installed for $627.

A regional breakdown of the 1936 heating-oil sales[5] indicates that the Middle Atlantic states (New York, New Jersey, Pennsylvania, Delaware, Maryland, and the District of Columbia) constitute the most important market for heating oils, and that this area accounted for nearly 39,000,000 barrels, or 39.3 percent of the 1936 total. The 1936 deliveries in this region represent a gain of 28.7 percent over the 1935 sales of 30,279,000 barrels. The North Central group of states (North Dakota, South Dakota, Minnesota, Nebraska, Iowa, Wisconsin, Illinois, Indiana, Michigan, Ohio, Kentucky, and Tennessee) wherein are located a number of important urban centers of population, such as Chicago, Detroit, St. Louis, Minneapolis, and Kansas City, ranks second as a consuming area for heating oils. Sales of heating oils in these states increased from 19,730,000 barrels in 1935 to 27,015,000 barrels in 1936. The latter total is 27.2 percent of all heating-oil sales for the year, compared with 25.7 percent in 1935.

The New England states stand third as a market for heating oils; they required 17,506,000 barrels in 1936, compared with 14,040,000 barrels in 1935. The remaining regions, i.e., South Central, Pacific Coast, South Atlantic, and Rocky Mountain, are of less importance as consuming areas for heating oils, and rank in requirements in the above order. It should be noted, however, that the South Central states became the fourth most important market for heating oils in 1936, supplanting the Pacific Coast area for the first time.

The following comments regarding the heating-oil market in the Pacific Coast area are credited to E. T. Knudsen of the San Francisco office of the U. S. Bureau of Mines:

"Demand for heating oils constitutes approximately 6 percent of the total domestic fuel-oil demand in the Pacific Coast area (California, Oregon, Washington, Arizona and Nevada) and is relatively of much less importance than in the balance of the United States as a whole. The comparatively mild climate and the large supply of natural gas in California tend to retard the growth of the use of oil for heating purposes, but during 1936 it is reported that sales of domestic oil burners increased appreciably in the Pacific Coast area, particularly in Oregon and Washington. In the Pacific Coast area it was not possible to obtain segregated heating-oil data showing the sales of lighter grades 1 to 4 and heavier grades 5 and 6, as was done in the balance of the country, partly because the Pacific Coast specifications of grades 1, 2, 3, and 4 do not coincide with the Eastern specifications, as grade 3 overlaps grades 4 and 5, and partly because the reporting companies do not yet consider this class of business of sufficient importance on the Pacific Coast to warrant the compiling of segregated data. Therefore, the sales by grades have been estimated."*

*See Table 10 for regional distribution of heating-oil sales, 1934-36. This table shows an increase of 29.1 percent in 1936 over 1935. The same table also shows an increase of 26.8 percent in range-oil sales during the same period.

SALE OF FUEL-OIL BURNERS

As is well known, the sales and operation both of domestic and industrial burners have rapidly increased since 1921. The number in operation has practically doubled since 1929, showing the industry to be almost "depression-proof." The reported number[6] of domestic burner sales for 1936 was 220,000, or an increase of 40 percent over the 1935 sales of 156,700. This number does not include range and space burners. These results look imposing, but the fact remains that they have sold only one oil burner to every 12 homes with central-heating plants in the United States. Last year the refrigerator industry sold 1,892,378 units, or approximately nine times the number of domestic oil burners sold. For the first seven months of 1937, some 1,898,656 refrigerators were sold, an increase of 15.2 percent over the same period last year. The new burner orders for the first eight months of 1937 totaled 118,821, as against 102,442 in the 1936 period; and shipments amounted to 116,159, as against 99,866 in the 1936 period. This indicates the total sales this year will exceed the 220,000 burners sold in 1936.

Table 8 shows an interesting comparison of burner sales, operation, and fuel consumption.

FUTURE BURNER SALES

The U. S. Department of Commerce recently completed a survey[7] of heating installations in 64 cities, and found that only 3.9 percent of all one-family houses were heated by oil. In this survey they covered 1,536,806 homes. They extended this survey to 1,931,053 residential structures and apartments in the same 64 cities, and found that 85,702 or 4.4 percent were heated by oil. These figures do not represent power burners

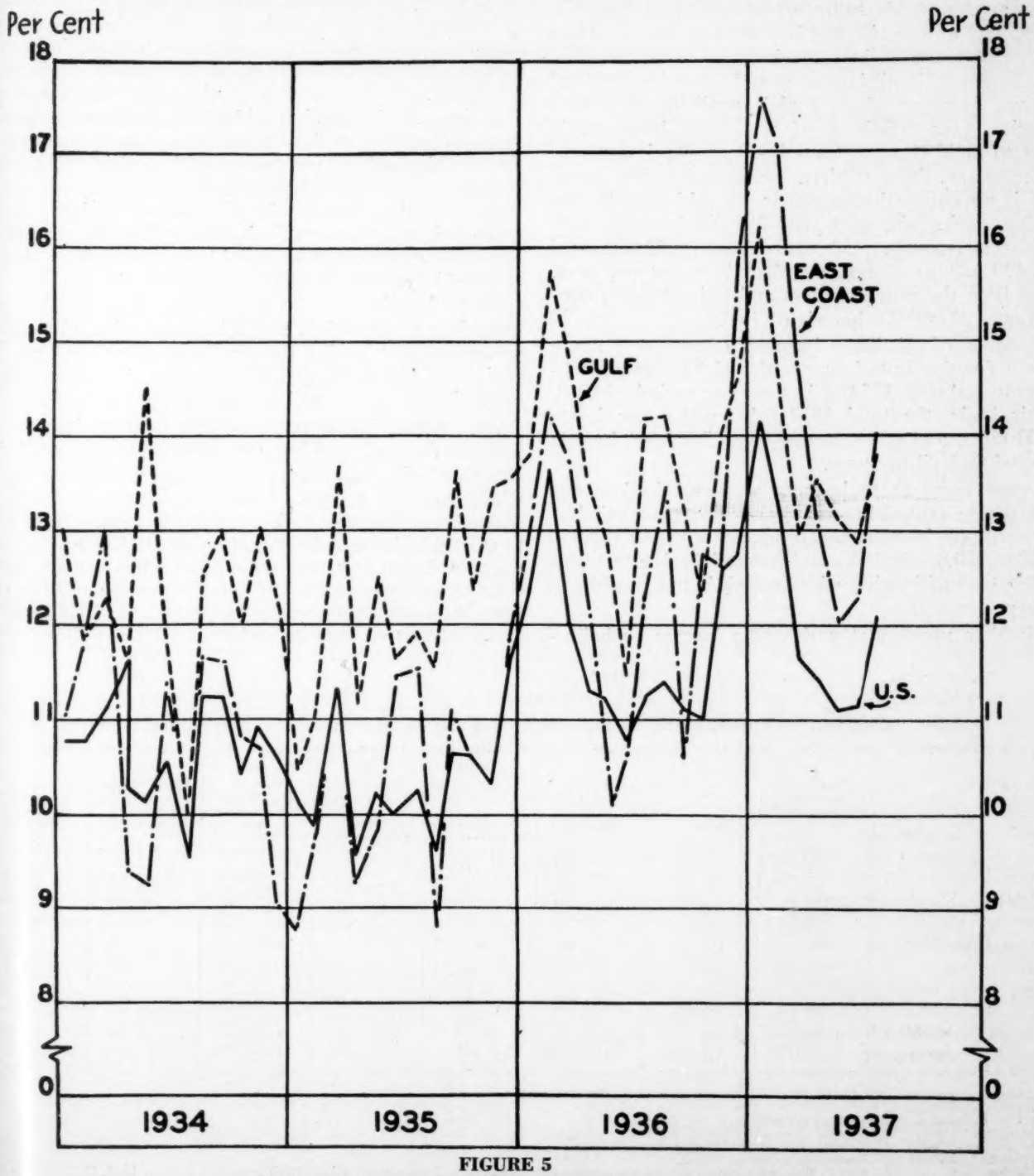


FIGURE 5
Yield of Gas Oil and Distillate Fuel Oil from Crude Oil.

Area	Percent Oil Burners to Total Structures	No Oil Burners
New England	19.5	33,819
Middle Atlantic	1.6	2,038
East North Central	1.1	4,190
West North Central	7.0	21,380
East South Central	0.1	162
West South Central	0.2	331
Mountain	1.4	1,276
Pacific	6.7	18,535
Total	4.4	85,702

alone, but in some areas the 4.4 percent included range-oil burners. The same survey showed the following percentages of oil-burner installations against total structures in various geographical areas:

No one expects that the oil-burner market will ever become as thoroughly saturated as has the automobile market. The automobile has become thoroughly established as a necessity in the minds of many families, while the domestic oil burner would often be classified as luxury in areas where coal is available at a very low price. Our definition of a luxury, however, is subject to rapid change; for a luxury today is a necessity tomorrow. The modern kerosene-burning space heater is an outstanding example, as evidenced by the fact that during the past year 391,696 burners were sold in this country. Each space heater will consume about 400 gallons of range fuel or kerosene per year. During 1936 the range burners and space heaters consumed over 27,000,000 barrels of fuel.

Shipments of distillate burners (range and space burners) for the first eight months of 1937 were 199,216, compared with 155,062 in the same period of 1936. On this basis, the total 1937 sales will approximate 500,000 units, and will consume some 5,000,000 barrels additional fuel oil per year.

In most cases these burners are used in low-cost homes where central-heating plants are not available. The number of these burners has increased from 127,197 in 1932 to 970,853 in 1936, which certainly demonstrates that this type of heating with fuel oil is not considered a luxury.

A further proof that a domestic burner or boiler-burner unit is not a luxury is brought out in a recent statement from a nationally-known burner company to the effect that "60 percent of the automatic-heating-equipment sales in 1936 were made to buyers with annual incomes between $1800 and $4500." A further evidence that burners are being installed in smaller homes is shown by a recent study of 100 installations which revealed that 90 percent were for capacities of less than 1½ gallons per hour, while a few years ago the average would have been 2½ gallons.

GRADE OF FUEL DEMANDED FOR BURNERS

From the data collected on quantities and grades of fuels used in the past, we obtain some indication as to future demands; but the two important factors which really determine the trend of the fuel-oil business are: first, the type of units the oil-burner manufacturers are selling and, second, the type of fuels refiners are developing for use in these units. After all, it is the type of burners that determines the grade of oil that must be used. We have seen changes in burner construction and changes in trend of popularity of different types of burners which caused the refiners to change the fuel-oil specifications to meet that particular demand. Going further than this, the refiners must analyze the course of development in the burner business, and point their efforts along the indicated lines. Such studies are quite essential when considering that many times changes in refinery operations require entire new equipment, and such changes consume several months' work in design, construction, and initial operation. Also, the refiners cannot justify the purchase of such expensive equipment unless the demand for a special product can be projected over a satisfactory pay-out period.

An outstanding example of the type of burner in popular demand, causing the refiners to change their entire fuel-oil schedule, occurred between 1932 and 1936, when the rapid growth of range or blue-flame burners necessitated the refiners increasing their kerosine yields to meet this demand. During the year 1936 some 390,000 range and space burners were sold in this country, and the average consumption of kerosine was about 400 gallons, or roughly, these stoves required 4,000,000 additional barrels of kerosine per year. Figure 1 shows that

TABLE 8

Sales, Operation, and Heating-Oil Consumption of Domestic Oil Burners in the United States

Year	(1) Burners Operating Beginning of Year	(2) Sales	(3) Total Burners	(4) Scrapped	(5) Burners Operating End of Year	(6) Average Number in Use During Year	(7) Heating-Oil Consumption (Barrels of 42 Gallons)	(8) Per-Burner Consumption (Barrels)
1921	12,500	9,000	21,500	.....	21,500	17,000	765,000	45
1922	21,500	35,300	56,800	.....	56,800	39,150	1,762,000	45
1923	56,800	43,000	99,800	.....	99,800	78,300	3,524,000	45
1924	99,800	79,700	179,500	800	178,700	139,200	6,264,000	45
1925	178,700	45,200	223,900 *a*	46,500	177,400	178,000	8,010,000	45
1926	177,400	77,700	255,100	12,000	243,100	210,300	8,905,000	42
1927	243,100	82,700	325,800	3,800	322,000	282,600	11,709,000	41
1928	322,000	107,500	429,500	5,400	424,100	373,100	14,272,000	38
1929	424,100	131,300	555,400	7,900	547,500	485,800	19,581,000	40
1930	547,500	126,400	673,900	8,800	665,100	606,300	25,771,000	43
1931	665,100	104,000	769,100	8,300	760,800	712,900	24,659,000	35
1932	760,800	86,200	847,000	3,800	843,200	802,000	32,814,000	41
1933	843,200	89,300	932,500	12,200	920,300	881,800	35,190,000	40
1934	920,300	110,100	1,030,400	16,300	1,014,100	967,200	40,472,000	42
1935	1,014,100	156,700	1,170,800	16,100	1,154,700	1,084,400	49,903,000	46
1936	1,154,700	218,500	1,373,200	22,000	1,351,200	1,242,000	59,616,000	48

a Large number scrapped due to failure of large manufacturer; burners removed for lack of service.

Sour(es of information!

Columns 1, 2, 5—Oil Burner Institute.
3—Columns 1 plus 2.
4—Estimated on basis of burners operating at end of year.
6—Average of columns 1 and 5.
7—1921 to 1925 estimated upon the assumption that the average burner used 45 bbl. of oil annually; 1926 to 1931, U. S. Bureau of Mines total heating-oil consumption figures and burners in use; 1936 estimated.

the total consumption of range fuel is more than 27,000,000 barrels per year. This demand for range fuel also changed the classification of fuels on the Eastern seaboard, as formerly kerosine was used largely for illuminating purposes and there was available a No. 1 fuel oil which met the "commercial standard specifications"; but, as is well known today, the No. 1 fuel oil on the East Coast was changed to a kerosine specification suitable for operation in a blue-flame or range burner.

The type of burners in use by the consumers will designate the grade of fuel that the refiner and distributor must handle. As it well known, the Underwriters' Laboratories in Chicago tests the various makes and models of burners and approves them for safety when using a particular number of grade of fuel oil. The "1937-38 Specification Chart of Oil Burners," *Fuel Oil Journal,* lists oil burners of 352 trade names and makes, and involves some 1108 models. This list, of course, includes burners which are several years old, thus accounting for the large number of models. The percentage of these models recommended for the various fuels is shown in Table 9.

If we consider separately the burners designated for domestic grade fuel, viz., fuel oils Nos. 1, 2, and 3, there is a total of 991 models. Again, grouping those designated for fuel oils Nos. 2 and 3 in one group, it shows that 88.1 percent could probably be operated on a single grade of fuel, and the balance could use a kerosine grade No. 1 fuel. Another interesting fact brought out by this table is that only 13 models, or 1.13 percent of the burners, are designed for No. 4 fuel. This figure is much lower than indicated by the volume of No. 4 fuel which has been distributed for domestic use, especially on the Atlantic seaboard. The No. 4 grade is not approved for domestic use by the underwriters.

The following figures[8] show the trend in conversion-burner types installed between 1932 and 1936:

	1932	1936	Average for 5 Years
	(All Figures in Percent)		
Vaporizing	9.0	1.4	3.5
Vertical rotary	19.0	9.3	14.6
Horizontal rotary	5.0	1.0	2.5
Pressure	67.0	88.3	79.4

These figures show that a combination of horizontal-rotary and pressure-type burners would total about 90 percent.

In many cases demands are made on the fuel supplier in order to obtain some selling advantage for a particular burner, such as a lower fuel price through a substitution of grades. The supply position has been complicated due to the use of gravity designations for fuel-oil grades rather than the use of "commercial standard numbers." This production with numerous grades was carried to a climax a few years ago when some of the pricing publications posted prices for 16 or 18 different grades of fuels, each separated by two points in gravity. Fortunately, most of the country has adopted the "commercial standard" designation for producing and marketing fuel oils. The only exception to this today is perhaps the Pacific Coast, where the nomenclature is somewhat different due to the fact that in many cases their domestic grade of fuel corresponding to No. 3 commercial standard is called Diesel fuel.

There is one definite way in which the oil burner industry and the fuel oil distributors can assist the refiners in producing an adequate supply of fuel oil at a fair price. This assistance should be in the form of an earnest endeavor to reduce the number of grades of fuel now demanded for tank wagon delivery. It is well known that we are operating in this country more than 28,000,000 automobiles of numerous makes and models on two primary grades of gasoline. It should be possible to operate all of the 350 different makes and models of domestic oil burners on two grades of fuel oil.

TABLE 9
Type Fuel Recommended for Various Models

Models			
Percent	Number	Recommended for:	Fuel Oil
10.23*	118		No. 1
10.06*	116		No. 2
65.65	757		No. 3
1.13	13		No. 4
4.34†	50		No. 5
8.59†	99		No. 6

*Of these models, 20 show recommendations for either No. 1 or No. 2.
†Of these models, 25 show recommendations for either No. 5 or No. 6.

The recommended grades which should suffice for all of the different makes of domestic burners would be:

1. A light fuel oil of kerosine quality for sleeve and pot-type burners and those few power burners which require a No. 1 grade.

2. A grade for domestic burners shown above as vertical-rotary, horizontal-rotary, and pressure-type. This could be accomplished by improving the present No. 3 grade by reducing the boiling range and by adding a carbon-residue maximum. This grade should suffice for about 90 percent of the domestic burners.

3. This grade would consist of a residue fuel suitable for commercial burners, and could have rather wide specifications so as to meet the particular needs; would replace the present 4 and 5 grades, and could be used without pre-heating.

It is somewhat more difficult to lay down exact specifications for commercial burners; because some of this type are equipped with pre-heaters, and others must be furnished an oil suitable for use without pre-heating. This simplification of fuel oil grades would eliminate refinery equipment, duplicate storage tanks and lines; simplify bulk transportation, bulk terminals, retail storage facilities, trucks, etc.

In order to operate successfully a large number of different makes and models of domestic oil burners on this limited minimum number of grades, it is absolutely essential that the product be of the highest possible quality.

The combination of a satisfactory oil burner and a satisfactory fuel oil creates a "domestic utility" which should deliver to the consumer the ultimate in heating happiness. This can only be attained through close cooperation between the oil-burner manufacturers and fuel-oil producers. The refiner has several responsibilities in the successful operation of this "domestic heat utility," and of first importance is the quality of the fuel oil. This statement needs no detailed proof, because we have all seen the difficulties resulting from poor-quality fuels due to improper refining or impurities acquired during transportation and storage.

FUEL-OIL SPECIFICATION COMMITTEES

Until a few years ago specifications of fuel oils were largely devised by each refiner to conform to his particular refinery operations; and, in many cases, had

TABLE 10
Regional Distribution of Heating-Oil Sales, 1934-1936*

(Thousands of Barrels of 42 Gallons)

Region	1934	1935	1936	Percent of Increase in 1936 Over 1935
Pacific Coast	4,347	5,586	6,525	16.8
Rocky Mountain	246	319	400	25.4
North Central	16,324	19,730	27,015	36.9
South Central	4,180	5,260	6,634	26.1
New England	10,793	14,040	17,506	24.7
Middle Atlantic	23,497	30,279	38,956	28.7
South Atlantic	1,435	1,639	2,213	35.0
Total United States	60,822	76,853	99,249	29.1

(Thousands of Barrels of 42 Gallons)

Regional Distribution of Range-Oil Sales, 1934-1936

Region	1934	1935	1936	Percent of Increase in 1936 Over 1935
Pacific Coast	459	548	596	8.8
Rocky Mountain	43	67	80	19.4
North Central	951	1,522	1,944	27.7
South Central	331	937	1,222	30.4
New England	9,912	12,530	14,505	15.8
Middle Atlantic	3,869	5,208	8,036	54.3
South Atlantic	191	714	909	27.3
Total United States	15,756	21,526	27,292	26.8

NOTE 1.—All the 1936 items shown in this report are preliminary, and are subject to revision.

NOTE 2.—The data for California, Oregon, Washington, Arizona, and Nevada were compiled by E. T. Knudsen, assistant economic analyst, U. S. Bureau of Mines, San Francisco, Calif.

* By A. T. Coumbe, associate economic analyst, Petroleum Economics Division, U. S. Bureau of Mines.

little or no regard for ultimate consumer requirements. After domestic fuel oils came into general use, it was found necessary to devise specifications, so that suitable fuel oils would be available for use in some 350 different makes and models of domsetic and commercial oil burners which are being used in this country today. It was also necessary to develop specifications for specialized uses, such as in Diesel engines, range burners, space heaters, tractors, and for unusual industrial purposes.

Specifications for fuel oil have been developed by the American Society for Testing Materials (D 396-34T), and these specifications have also been promulgated as "commercial standards" by the Division of Trade Standards of the Department of Commerce.

The active group for fuel-oil specifications in the American Society for Testing Materials is Technical Comimttee E of Comimttee D-2 on Petroleum Products and Lubricants. Technical Committee E was recently appointed on the reorganization of former Technical Committee C into separate committees on burner fuels and Diesel fuels. Technical Committee E is composed of representatives of producers of fuel oils and consumers—the latter group being represented in most cases by oil burner manufacturers, and this committee is now studying possible improvement in the specifications.

To advise the Division of Trade Standards in connection with future revisions of the Commercial Standard for Fuel Oils (CS 12-35) a standing committee has been appointed consisting of producers, distributors, burner manufacturers, users, consumers, and safety interests. Revisions are promulgated only after acceptance by 60 percent of the producing group.

After any change in the commercial standard for fuel oil it is customary for the Underwriters' Laboratories to test and re-classify burners according to the new specifications. The results of such a classification are given in Table 9.

At the present time the specifications have classified fuels into six grades, according to uses, as follows:

There are three grades of fuel oil recognized and recommended for domestic use. These grades are:

Fuel Oil No. 1
Fuel Oil No. 2 } Domestic Use.
Fuel Oil No. 3

For commercial use in hotels, apartment houses, office buildings, schools, churches, etc., the following grades are used:

Fuel Oil No. 4
Fuel Oil No. 5 } Commercial Use.

For industrial use in public buildings, steam generation in power plants, steamships, locomotives, industrial processes, etc., the following grade is used:

Fuel Oil No. 6 } Industrial Use.

FUTURE SUPPLY OF FUEL

After quality, perhaps future supply is the next important feature to consider.

Petroleum products are generally rated next to food, clothing, and shelter as essential to present-day living. This position in the scheme of human well being makes it natural that the public should be profoundly interested in the question of an adequacy of supply. Since the first discovery well in Pennsylvania in 1859, there have been innumerable warnings of petroleum scarcity. In the past 20 years the U. S. Geological Survey has made some 11 official surveys of the petroleum reserves, and usually the later estimates exceeded the earlier ones.

For several reasons the problem of petroleum reserves should not be a source of concern to those interested in the sale of oil burners and fuel oils. First, the geologist and engineer have replaced the old time prospector who located wells by means of the divining rod or intuition. The success of these modern methods is demonstrated by their uncanny ability to predict the presence of oil and the actual depth at which it will be found. Second, the modern refining methods have increased the yield of the more valuable products, as shown by the fact that in 1914 only about one sixth of a barrel of crude was converted into gasoline; while today, through cracking, polymerization, and other technical improvements, the average yield has been increased to 44 percent. It is estimated that cracking has conserved approximately 40 percent of the total crude run to stills in the past 16 years. Third, it is estimated the shale-oil reserves[9] located in our western states would be sufficient to supply our present rate of consumption for more than 100 years. This deposit is located largely in the Rocky Mountain states, and it is estimated it contains a potential supply of some 92,000,000,000 barrels of crude oil.

The proved reserves[10] of crude petroleum in the United States as of January 1, 1936, were estimated at 13,063,000,000 barrels of the standard 42 gallons. This estimate was prepared by a committee of geologists, geophysicists, and petroleum engineers selected by the American Petroleum Institute, and is unquestionably reliable.

SEASONAL DEMAND

In order to maintain a satisfactory, fuel-oil-gasoline supply-demand relationship, it will be necessary: 1, that the winter demand for gasoline continue to increase; 2, that in the process of meeting the seasonal demand for fuel oil an excess of gasoline is not produced.

It is quite apparent that both conditions (1) and (2)

TABLE 11
Comparison of Fuel-Oil Production—1934-35, 1935-36, 1936-37 *

(Figures in Thousands of Barrels)

Months	Production 1934-35	Production 1935-36	Increase 1935-36 Over 1934-35 (Percent)	Production 1936-37	Increase 1936-37 Over 1935-36 (Percent)
Gas Oil and Distillate Fuel:					
November	8,044	8,598	6.89	11,201	30.27
December	8,136	9,885	21.50	11,875	20.13
January	7,696	10,587	37.56	13,319	25.80
February	7,001	11,125	58.91	11,206	0.73
March	8,678	10,262	18.25	11,005	7.24
	39,555	50,457	27.56	58,606	16.15
Residual Fuel:					
November	19,917	23,660	18.79	23,671	0.04
December	21,086	25,043	18.77	25,670	2.50
January	20,545	24,573	19.60	25,453	3.58
February	19,480	23,751	21.92	22,222	−6.44†
March	20,822	23,667	13.66	25,081	5.96
	101,850	120,694	18.50	122,097	1.16
Total Fuel Oil:					
November	27,961	32,258	15.37	34,872	8.10
December	29,222	34,928	19.53	37,545	7.49
January	28,241	35,160	24.50	38,772	10.27
February	26,481	34,876	31.70	33,428	−4.15†
March	29,500	33,929	15.01	36,086	6.36
	141,405	171,151	21.02	180,703	5.58

* U. S. Bureau of Mines.
† Denotes loss.

TABLE 12
Deliveries of Fuel Oils by Months

(Figures in Percent)

	September	October	November	December	January	February	March	April	May
Kerosine	6.1	8.3	9.5	13.0	13.0	13.1	9.6	9.1	5.4
Fuel oil	4.1	7.2	9.1	17.3	18.4	17.7	9.4	7.1	3.2

NOTE.—These percent delivery figures are corrected to average normal temperatures taken from average degree-days for the past several years.

are greatly affected by the unpredictable factor of weather. Thus the winter 1936-37 was unusually mild (about 9 percent less degree-days in New York area) which permitted a higher level of gasoline consumption and required less current winter production of fuel oils. Table 11* shows a comparison of fuel-oil production for the past three heating seasons during winter months. This shows an increase in distillate fuels of 27.56 percent in 1935-36 severe winter season as compared with previous season, and a total increase of all grades of fuel oils of 21.02 percent. For the season 1936-37, with a milder winter, this yield over previous season decreased to 5.58 percent, which was more in line with increase created by additional burner installations. The decreased production of residual fuel oils in 1936-37 is more pronounced than for distillate fuels.

EFFECT OF WEATHER ON DEMAND

Both the fuel-oil producer and the fuel-oil distributor have difficulties in balancing the production against demands because of the unpredictable weather feature. It is not generally recognized that, for a normal heating season, the distributor must be prepared to deliver approximately 53 percent of the total season's requirements in the months of December, January, and February, while the balance is consumed over an additional six-months' period. In the case of kerosine or range fuel, the distributor must be prepared to deliver approximately 39 percent within the same three months, but this peak demand is not so apparent because kerosine or range fuel is used throughout the year for cooking in addition to heating. Table 12 shows deliveries of fuel oils by months, and the figures are corrected to average normal temperatures taken from average degree-days for the past several years in the New York area.

In addition to being required to deliver some 53 percent in a three-months' period, this percentage is estimated to be normal, and can be increased or decreased as much as 15 percent above or below the normal figure by the uncontrollable weather factor. This means that the 53 percent can be increased to 60 percent with sub-normal weather conditions. These percentage deliveries by months are very useful in projecting sales demands.

Because of the fact that it is not possible to change over refining operations to produce only fuel oil during any period, the refiners must project their production schedule several months ahead of the actual demand. Because of seasonal demand and rather concentrated consumption in metropolitan areas, a considerable volume of the fuel oil must be stored at the point of consumption. This is especially true on the Eastern seaboard where much of the fuel oil is produced in the Gulf, and must be transported in tankers operating under regular schedule. This peak-demand feature is just another one of the petroleum refiner's and producer's problems brought on by the weather man.

THE FUEL-OIL DISTRIBUTOR

Fuel-oil distribution has a very important part to play in establishing successful "heat service" for the customer. The importance of a quality fuel oil has already been discussed; and, in addition, the fuel-oil distributor has added several desirable service features for the domestic customer. First is the automatic delivery, or "keep-filled-service," which places on the distributor the responsibility for maintaining an adequate supply of fuel oil in the customer's tanks re-

*U. S. Bureau of Mines.

gardless of weather conditions. This function is carried out by one or more operating methods, such as route delivery, whereby the customer is visited at regular intervals, or by use of tank checkers who measure fuel in customers' tanks and route delivery trucks accordingly. The latest and most successful method is by use of the "degree-day delivery system."[12] This method is not complicated, and affords a definite advantage to the customer and lower delivery costs to the distributor. The use of any one, or a combination of these systems, eliminates the problem of constant supply from the customer's mind, and takes away from the gas company the most popular argument against the use of fuel oil.

The distributor now utilizes meters for fuel-oil deliveries, thereby eliminating any question as to volume delivered, and places the measurements on a par with gas and electric deliveries. In addition to meters, some of the fuel trucks are now equipped with printing devices which print on the customer's delivery receipt the actual number of gallons delivered. All of these service features furnished by the fuel-oil distributor certainly assist in selling oil burners and in keeping them sold to present users.

Certainly, many householders are "automatic-heat" conscious today; yet in the United States there is only one oil burner installed to every 12 homes with central-heating systems. The demand for heat is a recurring necessity, and their "heating dollar" is now in circulation and will go to the distributors who provide the most satisfactory "heat service."

CONCLUSION

The market for domestic oil heating, the greatest contributor to human comfort and convenience, has hardly been furrowed, It has been shown how the very rapid installation of oil burners in the past few years has changed the refiner's production schedule and, further, that an adequate supply of fuel oil has been and will be available to the consuming public at a reasonable price. There is, however, one definite way in which the oil-burner industry and the fuel-oil distributors can assist the refiners in producing this adequate supply of fuel oil at a fair price. This assistance to the refiner should be in the form of an earnest endeavor by these interested parties in reducing the number of grades of fuel oils now demanded for tank wagon deliveries. It is well known that we are operating in this country more than 28,000,000 automobiles of numerous makes and models on two primary grades of gasoline. It should be possible to operate all of the 350 or more different makes and models of domestic oil burners on two primary grades of domestic fuel oil. The commercial burners operating automatically and without pre-heaters should be supplied with a grade to meet this service, and still another grade of heavier fuel should be available for industrial use. With this reduction in the number of grades of fuel oil to a total of four, the refiners can use their full efforts in producing quality fuel oils in volumes sufficient to meet the increasing demands.

It is recognized that fuel oil must be inexpensive enough to stimulate the sale of oil burners, and must be generally available; and, finally, there must be a sufficient demand for standardized products to interest the petroleum industry in its production and distribution. The petroleum industry fully realizes the importance of producing fuel oils for this rapidly-expanding market, and has been rewarded for this service by an increase in the number of satisfied customers and an unprecedented increase in sales volume.

Finally, when we consider the magnificent technical improvements made in late years in the production, refining, and utilization of fuel oils and their adaptation to the services of mankind, we can look into the future with complete trust in the continued development of this important part of the petroleum industry.

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Aircraft Operation With Fuels of 100 Octane Number and Higher

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AN ATTEMPT is made to survey the present state of knowledge of the application of 100-octane aviation fuels. Known engine effects and likely effects of 100-octane fuels on airplane performance are discussed, and the somewhat controversial matter of effect on earning capacity of commercial transport airplanes is surveyed mostly in the light of present theoretical estimates. Actual commercial operating data with 100-octane fuel are not available, and the effects on earning capacity will not become definite until such data are obtained.

Rather elementary discussion of the effects of increased engine power on airplane take-off, airplane design, and airport size are presented. The importance of reduction of cruising fuel consumption on airplane range and payload is stressed.

Data are presented on engine performance with fuels of over 100 octane number, and it is concluded that the trend will be for octane numbers to go over 100 in the future.

This paper was presented at Eighteenth Annual Meeting, American Petroleum Institute, Chicago, November 12, 1937.

1. INTRODUCTION

THE constant increase in specification requirements of petroleum products for aircraft-engine use has often been a thorn in the flesh of the manufacturing departments of the oil industry. The refiner is at times inclined to regard the demands for products which are increasingly difficult to produce and steadily more costly as unjustifiable whims of the aircraft industry. That the developments of the last 10 years, which have turned commercial aviation from a struggling infant into a fairly mature adult, are due in no small measure to improved petroleum products is not generally appreciated in the refineries. The use of 70 octane fuels in most modern multi-engine transport aircraft would preclude the carrying of any payload.

It would appear that the trend of aircraft fuels is bound to be in the direction of a progressive steady increase of octane number. This will involve the use of synthetic fuels which many refineries cannot manufacture economically at present. Refiners who assume that the present trend of octane numbers is evidence of unsound development methods on the part of the aircraft industry would seem to be due for a rude awakening.

In this paper an attempt will be made to survey: history of fuel and concurrent engine development, effect of octane number on engine performance, relation of engine and aircraft performances, and the relation of engine performance to aircraft earning capacity.

2. FUEL DEVELOPMENT AND ITS PAST INFLUENCE ON ENGINE DEVELOPMENT

In 1928 fuel of 50 octane number was in general service use, but was found to have destructive effects on the larger air-cooled engines. Attempts to control anti-knock value were ineffective until the octane-number scale was adopted in conjunction with standardized knock-test methods. These knock-test methods gave results which were reliable indices of full-scale engine behavior only in the case of straight-run gasolines, either clear or blended with lead. With the establishment of a workable method of defining fuel anti-knock quality which gives a reasonably accurate index of full-scale engine value, the possibilities of increased engine performance with the higher octane-number bracket soon became generally appreciated. The U. S. Army Air Corps standardized 87-octane fuel (about 84 ASTM octane number) for all uses except training, and 73 and 80 octane numbers soon became standard for commercial use. Fuel of 87 ASTM octane number came into limited commercial use for take-off purposes. With the introduction of the Douglas DC-2 airplane, 87 octane take-off fuel came into general commercial use in conjunction with 80 octane fuel for cruising. In general, engines using 87 octane take-off fuel and 80 octane cruising fuel in commercial service were, and are, so supercharged that the normal cruising power can be maintained up to an altitude of about 12,000 feet, beyond which it begins to fall off. There is now a general demand for the maintenance of normal cruising power to higher altitudes, and engines are now so supercharged that cruising power can be maintained to an altitude of about 15,000 feet, and this has resulted in the use of 87 octane fuel for cruising. The demand for minimum fuel consumption at the cruising condition has also been a contributing factor in the use of 87 octane fuel for cruising. Take-off fuel of 90 ASTM octane number is now in limited commercial use.

Fuels up to 87 octane number with 3 cc. lead can be generally produced from selected straight-run naphthas. Fuel of 90 ASTM octane number, with 4 cc. lead, can be produced from straight-run naphtha. When more than 87 octane number is required with a 3-cc. lead limitation, the use of synthetic blending agents then becomes essential.

Results of tests with 100 octane (Army method) fuels by the U. S. Army Air Corps were given early in 1935 by Klein.[1] Most of the fuels tested contained com-

mercial *iso*octane, and the results served to show the possibilities of increased engine performance with fuel octane numbers in excess of the then current 87 ASTM. However, 100 octane fuel has as yet had only very slight commercial use, although it appears inevitable that it will come into such service on account of the demands for maximum take-off power and minimum specific fuel consumption at cruising. The aircraft-users' demands for take-off power and cruising economy apparently can only be met with 100 octane fuel even with the most advanced of available engines.

Special aircraft engine fuels, usually containing alcohols and high percentages of aromatics and producing abnormally-high performance for racing and other stunt purposes, have been used in the past; but, apart from cost and limited supply, such fuels have had limitations which made them considerably inferior to normal 87 octane fuels for general service use.

The advent of 100 octane fuels using *iso*octane, blended with straight-run gasoline as a base, resulted in a high-octane fuel which was free of the operating disadvantages of the stunt type of fuel. Fuel blends of 100 octane number, containing *iso*octane, can be used with the same operating technique that is observed with current fuels using gasoline alone as a base. With *iso*octane-gasoline blends the problems of storage, contact with water, fuel-tank capacity, fuel-system and carburetor freezing, and carburetor settings are essentially the same as those involved with the use of gasoline.

Blending agents other than *iso*octane are available for the production of fuel blends of 100 octane number or more. *Iso*octane, however, is the only blending agent with any considerable background of service use, and the following discussion of high octane fuels is confined to blends made with *iso*octane as the major base blending agent. Limitation of discussion to *iso*octane blends does not infer that other blending agents have not a present wide field of application or may not have wide use in the future. While the discussion is limited to *iso*octane blends, it should be noted that such blends generally contain *iso*pentane, which gives the finished blend volatility characteristics similar to the present types of aviation gasolines.

At least half of the improvement in aircraft engine performance in the last 10 years is due to increase of fuel octane number[2] and to the use of the octane-number scale in conjunction with methods of measuring octane number, which result in any given grade of fuel giving substantially uniform service performance in any given engine type. High-octane fuels would be of little value if the effective full-scale engine octane number was subject to considerable variation from batch to batch.

Aircraft engines can be designed for satisfactory operation on 50 octane fuel. The Curtiss D-12 water-cooled 12-cylinder engine and many 200-horsepower air-cooled training engines have given very satisfactory results on fuel of 50 to 55 octane number. It is probable that aircraft engines can be produced which will develop 50 percent more mean effective pressure on 50 octane fuel than do present automobile engines on 70 octane number. There is no question, however, that such engines are not, and would not be, acceptable for high-performance aircraft use as long as the present type using high-octane fuels is an available alternative.

Aircraft is only able to compete with other forms of transportation by virtue of its performance. Point-to-point speed and ability to reach high altitude are the major items of aircraft performance by means of which it successfully competes with other forms of transport. From the military standpoint 60 miles per hour airplanes might have a limited field if they could reach any given altitude more rapidly than a balloon, but such a speed entirely eliminates the airplane from true commercial use.

It has been argued that the aircraft industry is obtaining increased output and performance by the use of higher octane numbers rather than pursuing the apparently sounder course of obtaining high output and performance with fuels of about 70 octane number; 1500 horsepower per engine is now available with 100 octane fuel, and it would take at least two years to develop an engine to give the same output on 70 octane fuel, even if all restrictions as to size and weight were removed.

While engine development may result eventually in obtaining the same over-all performance on 70 octane fuel as is now obtained with 100 octane fuel, such a result is at best problematical, and the aircraft industry wisely took advantage of a proven improvement rather than spend largely in time and effort attempting to secure a probable but uncertain result.

The aircraft-engine industry is continually striving for the production of increasingly-powerful engines, as witnessed by the introduction of 1400-1500 horsepower engines this year in this country. However, the production of more power by the mere increase of cylinder capacity sometimes results in increased engine power without increase of aircraft performance. In addition, large increase in engine-cylinder capacity, as a means of obtaining increased power, may result in a much greater increase of over-all cost of development than the use of higher-octane fuels, since the engine industry is not always on sure ground when jumping from an existing engine type to one with 30 percent greater cylinder capacity.

3. THE EFFECTS OF OCTANE NUMBER ON ENGINE PERFORMANCE

The more important effects of octane number on engine performance will be surveyed in the following discussion. The wide difference in engine and fuel conditions at take-off and cruising operation is not usually understood by those outside the aircraft field. It is often assumed that the best specific fuel consumption the engine will give is obtained at its maximum possible mean effective pressure. Thus, a mean effective pressure of 200 pounds per square inch is often associated with a specific fuel consumption of 0.40 pounds. Both of these are possible in some engines, but not simultaneously.

a. Relation of Take-off to Cruising Conditions

Since at the take-off condition the maximum possible power is required, all available methods of increase are resorted to. Detonation or other forms of uncontrolled combustion are most likely to occur in the range of air-fuel ratios between that giving maximum power and that giving complete combustion. It has been found that high fuel consumption will, within limits, make possible the same power output as is available with a higher-octane fuel running leaner. Thus, Klein[3] reports sensibly similar output and cylinder temperature on 92 and 100 octane fuels, with the latter having a 19 percent lower specific consumption. Rich mixture in lieu of high octane number has its limits, however, since excessive loss of power occurs if carried too far. For take-off at present, mixtures somewhat richer than those giving maximum power are general. Specific fuel consumption at take-off is quite generally as high as 0.7 pounds per brake horsepower hour, but this is unimportant since the total quantity of fuel used in the take-

off and initial portion of the climb is quite small in comparison with the total fuel load. The cruising power is generally of the order of 60 percent of the take-off power, the mean effective pressure being about 75 percent of that at take-off. Since at the cruising condition, both mean effective pressure and mixture temperature are lower than at take-off, the stress on the fuel is much reduced, and air-fuel ratio can be considerably increased. In present practice, cruising consumptions in flight of less than 0.45 pounds per brake horsepower hour are reported.

b. Power

Klein[1] in the first published performance data on comparison of 100 octane (Army method) fuel vs. 92 octane (Army method—aprpoximately 87 ASTM) fuel showed that the permissible increase of power was 12 to 30 percent, depending on engine type and operating conditions.

DuBois and Cronstedt,[4] using a supercharged full-scale single-cylinder engine, found that technical *iso*-octane permitted 17 percent more power output than 92 octane fuel (Army method—approximately 87 octane number, ASTM).

Current model engines in the 1000-1500-horsepower class have 15 to 20 percent higher take-off ratings with 100 octane fuel than with 87 octane.

DuBois and Cronstedt[4] have shown that *iso*octane plus 3 cc. of lead will allow an output increase of more than 17 percent over that available on *iso*octane alone. Klein[3] has shown that *iso*octane plus 3 cc. lead will give 55 percent more power than *iso*octane alone. Studies in a supercharged engine in the laboratories of Ethyl Gasoline Corporation have shown that fuels of over 100 octane number may give more than 160 percent of the power available on pure *iso*octane, or 250 percent or more of that available on 70 octane fuel.

c. Fuel Economy

Young[5] has shown that a specific fuel consumption of 0.35 pounds per brake horsepower hour can be obtained on the dynamometer with a large air-cooled engine operated at essentially cruising conditions on 100 octane fuel. This engine had a compression ratio of 7.85 to 1 in order to obtain the maximum fuel economy with 100 octane fuel. A similar engine, with a 6.4 to 1 compression ratio and using 92 octane (Army method) fuel, gives a best fuel economy of about 0.42 pounds per brake horsepower hour. The engines with 7.85 to 1 and 6.4 to 1 compression ratios have about the same available take-off powers on the fuels they are designed for, viz., 100 and 87 octane number.

Klein[3] has reported comparisons of 100 and 92 octane (Army method) fuels using the same type of engine as that discussed by Young[5]. Klein's engine had a compression ratio of 6.45 to 1; but, owing to differences in operating conditions and possibly owing to slight design modifications, gave much higher cylinder temperatures than shown by Young's data for the same compression ratio, at essentially similar output and revolutions per minute. At an output of 565 to 570 horsepower, Klein's data indicate that the minimum specific fuel consumptions just avoiding detonation are approximately 0.55 and 0.68 pounds, respectively, for 100 and 92 octane fuels. Thus the difference in fuel consumption at fixed compression ratio and output is approximately 19 percent lower for 100 octane than for 92 octane fuel. Young, by varying compression ratio to secure maximum economy at about the same power as Klein, with 92 and 100 octane fuels obtained a reduction in consumption of about 17 percent for the 100 octane fuel.

In general, the reduction of consumption that may be expected as a result of the use of 100 octane fuel in place of 87 octane (ASTM) is at present the subject of considerable discussion, with various estimates being used for the purpose of calculation. As Young has pointed out, it is not now possible to cruise engines in flight at the minimum consumptions obtainable on the dynamometer. However, with accurate measurement of both fuel flow and power[2] in flight now possible, cruising consumption in the air may be expected to become increasingly closer to the optimum dynamometer possibilities. It is the author's opinion that 100 octane engines, suitably installed and operated, may be expected to give between 10 and 15 percent lower consumption than equally efficient equipment designed for 87 octane (ASTM) fuel. Thus, if 0.44 pound per brake horsepower hour is being achieved with 87 octane fuel, 0.38 to 0.40 pound may be expected with 100 octane fuel. If existing 87 octane equipment is being operated under too severe cruising conditions, the substitution of 100 octane fuel without equipment change may well be expected to render possible a fuel consumption reduction of more than 10 to 15 percent.

That leaning off the air-fuel mixture is, in general, more important in securing reduction of fuel consumption in aircraft engines than is compression ratio, is not usually appreciated outside the aircraft-engine field, In the past in the aircraft-engine field, and at present in other engine fields, reduction of consumption by leaning off the mixture has been avoided on account of exhaust-valve burning and other troubles. Browne[6] was the first to emphasize the relative effects of mixture strength and compression ratio on fuel economy, and his remarks were startling to many engineers not familiar with aircraft-engine practice.

Mead[2] has stated that cruising at extremely low fuel consumption is the most critical condition that modern engines have to meet. Until demand for minimum cruising consumption became pronounced, the take-off condition was much the more critical than cruising.

Thus, the gains in engine performance due to 100 octane fuel in place of 87 octane fuel may be summarized as: a power increase of up to 30 percent, reduction of cruising fuel consumption of 10 to 15 percent, and the probable attainment of cruising fuel economy closely comparable with that of a compression-ignition engine.

4. THE EFFECTS OF OCTANE-NUMBER INCREASE ON AIRCRAFT PERFORMANCE

Experience is now sufficiently extensive that the engine effects of octane-number increase can be foretold within limits. From the change of engine performance, the effect on aircraft performance can be fairly definitely predicted. The effect of octane-number increase on earning power of commercial aircraft is much more indefinite than the change in aircraft performance. Several mathematical surveys of the economic value of 100 octane fuel vs. 87 octane fuel have been made, and arrived at widely different answers.

Some rather elementary discussion of the effects of engine performance of modern aircraft operation is thought to be justified at this stage.

a. Speed

The direct effect of power on speed at any given altitude is slight. Thus, a 10 percent increase in power at the best produces only a 3 percent speed increase, and usually considerably less than 3 percent. While the direct effect of power on speed at any given altitude is slight, the effects of maintaining power to increasing

altitude has had very large effects on speed. If engine power is held constant, irrespective of altitude, the airplane speed increases with altitude due to reduction of resistance as the air density falls off. Thus, when density has been reduced to 70 percent (approximately 10,000 feet) of that at sea level, airplane speed will have increased by about 20 percent. The modern clean airplane, equipped with flaps and controllable pitch propellers and having high wing loading, achieves with relatively-low engine power remarkable cruising speed at altitudes of 10,000 to 15,000 feet. In general, as the altitude to which a given power must be maintained is increased, so are the octane-number requirements raised. The reduction of air density with increase of height is counteracted by more supercharging. This usually involves higher mixture temperature and greater indicated power, both of which increase the stress on the fuel.

b. Take-off

With current land-plane types, the critical condition of power requirement is at take-off—since it is necessary to secure sufficient ground speed for the ship to become air-borne and to have a sufficient rate of climb to be able to gain altitude sufficient to clear obstacles at the boundaries of modern major airports. Barnard,[7] in a recent survey, has shown that modern land-transport airplanes have an average take-off weight of 13 pounds per take-off horsepower.

The high speed of modern aircraft is to a very considerable extent the result of the large increase in take-off power produced by recent engine, propeller, and fuel improvement and, particularly, to the constant-speed propeller which enables the engine to develop its full take-off power throughout the take-off run and the initial portion of the climb. The great increase in effective available take-off power in recent years has resulted in high-speed designs of aircraft which could not have taken off with the older-engine and propeller equipment.

Increased take-off power may find its greatest value in reducing the length of the take-off run and distance traveled before an obstacle of given height can be cleared. One large aircraft operator has calculated that, in the case of large multi-engine transports, a 20 percent increase in take-off power will reduce by 45 percent the distance necessary to take off and reach a height of 50 feet. On these figures it is indicated that, if a change from 87 to 100 octane fuel produces a 20 percent gain in take-off power, a ship using 100 octane fuel can obtain the same standard of safety in take-off from a 180-acre airport as given by 87 octane fuel from a 600-acre airport (both airports rectangular and geometrically similar). The problem of take-off has become sufficiently critical to warrant consideration being given to either a considerable increase in airport size or the use of catapulting.[8, 9] The area and cost of airports usually increase sensibly as the square of the length of the take-off runway, and airport costs are already very high. Hence, it would appear that engine or fuel developments which result in rendering available increased power for the short period necessary for take-off are likely to have very considerable economic value. Catapulting of land airplanes will, of course, involve considerable expense, and further limits operations to and from airports equipped with catapults.

Catapulting of seaplanes is already in use in experimental transatlantic air service. It would seem obvious that the investment in and operating cost of catapult mother ships must be so high that take-off fuels costing as much as $50 a gallon would be economically justified if they rendered possible an unassisted take-off.

In seaplanes and flying boats, the take-off condition is somewhat less critical than in land transport—since the allowable take-off distance is not, as a rule, affected by obstacles surrounding the take-off course. No matter what the length of run available, however, take-off time or distance is limited by the fact that the engine overheating will occur if the take-off run at low air speed is extended beyond certain time limits peculiar to each installation. In flying boats, increase of take-off power would appear to be essential in many cases of very long-distance non-stop operation, where crew, fuel, oil, and equipment loads now represent 90 percent or more of the disposable load.

c. Fuel Consumption and Range

Increase of fuel octane number may be used to increase airplane range by three methods:

1. The first is to increase the available take-off horsepower by more supercharging at take-off, thus allowing a greater fuel load to be carried. In this case reduction of specific fuel consumption at cruising may or may not be obtained, depending on the severity of the engine operating conditions.

2. In the second case the engine compression ratio is increased to give minimum possible fuel consumption available with the fuel to be used at the required cruising power. In this case the compression ratio is likely to be increased to the point where take-off power is no greater than that obtained with the formerly-used lower-octane fuel and engines with lower compression ratio.

3. The third method involves increase of compression ratio and take-off power, the compression ratio being increased sufficiently to have a noticeable effect on cruising fuel consumption and yet permitting a considerable increase in take-off power.

It is the author's opinion that the third method is most likely to be followed in the immediate future when new airplanes are being produced for use with 100 octane engines.

In some equipment now in service, and operating over short distances where fuel load is not significantly affecting payload, there is no doubt that safety would be increased by the use of take-off fuel of more than 87 octane number. However, this would involve the use of a double fuel system, which is not always conisdered desirable.

5. EARNING CAPACITY OF COMMERCIAL AIRCRAFT

Bass[10] has made mathematical investigations of the effects of 87 and 100 octane fuels on earning capacity of transport airplanes at 100 percent load capacity. The first type of investigation deals with the case of an existing airplane fitted with 87 octane engines which are to be replaced with 100 octane engines of the same take-off power. The 100 octane engines have their cylinder capacity reduced (apparently by 20 percent) and their specific weight is 9½ percent less than the 87 octane engines. The cruising specific fuel consumption is 9½ percent less with 100 octane fuel than with 87 octane. With assumptions of 25 cents per U. S. gallon as the cost of the 87 octane fuel and payload values of $0.000385 and $0.00077 per pound-mile (approximately 7½ cents and 15 cents per 200-pound passenger-mile) at a cruising speed of 160 miles per hour, the premium values of 100 octane fuel found are as shown in Table 1 for various flight ranges.

If Bass' data are re-calculated—substituting payload revenues, 87 octane fuel costs, and fuel gravities which

approximate the average in this country—the premium values become as shown in Table 2. In calculating Table 2, 87 octane fuel costing 15 cents per U. S. gallon, payload values of $0.00025 and $0.0005 per pound-mile (5 cents and 10 cents per 200 pounds passenger-mile), and fuel gravities of 70 A.P.I. for both 87 and 100 octane fuels have been assumed. The 20-hour-range condition dealt with by Bass closely resembles a 2300-mile non-stop transoceanic flight with 40 percent reserve fuel.

Bass also considers the case of the relative carrying power of an 87 octane airplane and a 100 octane airplane, both with engines which are similar in cylinder capacity and other respects, except output and cruising consumption. For the 100 octane engine the take-off power is increased 20 percent, the specific cruising fuel consumption reduced by 9½ percent at 20 percent increased cruising power. The specific weight of the 100 octane engine is assumed to be decreased by 9½ percent—the actual weight, therefore, being about 9½ percent more than the 87 octane engine. With other assumptions as to fuel cost, fuel gravities, etc., similar to those used in Table 1, Bass concludes that the premium values of 100-octane fuel for various flight ranges are as shown in Table 3.

Barnard[7] has made an extremely comprehensive investigation of the effects of octane number on earning power with the aircraft loaded to capacity. The effects on payload of increased take-off power obtained by raising boost and of increasing compression ratio, the latter reflected only in reduced cruising fuel consumption without change of take-off power, are examined. The investigation is based on earning power per pound (or gallon) of fuel, and the earning power resulting from any octane-number change is not related to any particular basic cost for, say, 73 or 87 octane fuel. The basic equation used credits increased take-off power with either a large and heavier airplane or, conversely, only a fraction of the increased load taken off is considered as disposable load. Calculated data showing the effects of specific payload revenue (dollars per pound-mile) and a range of disposable loads (disposable load equals crew plus oil and fuel plus revenue load) per available take-off horsepower are included. Amongst the most important of Branard's findings are the following:

1. That the change of earning capacity per octane number varies from about 2¼ cents to 8 cents per gallon, depending on operating conditions.

2. Earning capacity per octane number is proportional to specific payload revenue.

3. Range has only a slight effect on the earning capacity per octane number.

4. That increase of compression ratio to obtain minimum cruising fuel consumption and increased take-off power obtained by added supercharging, without affecting cruising fuel consumption, have sensibly equal effects on the incremental earning power per octane-number increase.

5. "The indicated increases in earning power are so much greater than any probable fuel-cost increases that the upward trend of octane-number requirements and use is clearly evident."

Keith, Carey, and Ward[11] have examined the earning capacities of 87 and 100 octane fuels in existing aircraft on a 720-mile non-stop flight. The relative earning capacities of the two fuels are considered on a basis of cruising specific fuel consumption. The airplane has a maximum permissible take-off weight, and reduction of fuel consumption enables more payload to be carried. The 87 octane engines are assumed to be replaced with 100 octane engines, and the latter are assumed to give a 15 percent reduction in specific cruising fuel consumption, and take-off and cruising powers are assumed to be the same for both engine types. The decreased fuel consumption with 100 octane fuel is considered in terms of its value from zero to 100 percent load factor, i.e., from no passenger, mail, or express load to maximum allowable take-off weight. Various distributions of load factor, such as half the flights with no payload and half with capacity payload, are examined. Keith, Carey, and Ward make the point that increased earning power based on capacity payload can never be fully realized in practice. On the above bases it is calculated that the payload may be increased by 11 percent by the use of 100 octane fuel, and that as long as the payload does not exceed 90 percent capacity (on 100 octane fuel) the earning power of the 100 octane fuel is only 2.1 cents per gallon more than that of the 87 octane fuel. As the payload increases beyond 90 percent, the incremental value of 100 octane fuel becomes greater—reaching 25.5 cents per gallon with the airplane fully loaded. If only 10 percent of the flights are made with capacity load, the incremental value of 100 octane fuel becomes 4.5 cents per gallon.

The opinion is expressed that due to fixed charges, etc., of the potential increased payload revenue, only 25 percent can be credited to the fuel. This, together with the savings in total fuel consumption, gives a net

TABLE 1

Range Hours	Payload Revenue (Dollars Per Pound-Mile)	Premium—Per Cent Cost of 87 Octane No.	Premium—Dollars Per U. S. Gallon Over 87 Octane No.	Premium Cents Per Octane No.
0	$0.000385	63	$.16	1.2
0	0.00077	121	.30	2.3
4	0.000385	122	.31	2.4
4	0.00077	240	.60	4.6
8	0.000385	182	.46	3.5
8	0.00077	360	.90	6.9
16	0.000385	300	.75	5.8
16	0.00077	600	1.50	11.5
20	0.000385	360	.90	6.9
20	0.00077	716	1.79	13.8

TABLE 2

Range Hours	Payload Revenue (Dollars Per Pound-Mile)	Premium—Per Cent Cost of 87 Octane No.	Premium—Dollars Per U. S. Gallon Over 87 Octane No.	Premium Cents Per Octane No.
0	$0.00025	71	$.11	0.8
0	0.0005	133	.20	1.5
4	0.00025	134	.20	1.6
4	0.0005	259	.39	3.0
8	0.00025	197	.30	2.3
8	0.0005	385	.58	4.4
16	0.00025	323	.49	3.7
16	0.0005	635	.96	7.4
20	0.00025	386	.58	4.5
20	0.0005	760	1.14	8.8

TABLE 3

Range Hours	Payload Revenue (Dollars Per Pound-Mile)	Premium—Per Cent Cost of 87 Octane No.	Premium—Dollars Per U. S. Gallon Over 87 Octane No.	Premium Cents Per Octane No.
0	$0.000385	710	$1.78	13.7
4	0.000385	650	1.63	12.5
8	0.000385	595	1.48	11.4
16	0.000385	478	1.19	9.2
20	0.000385	420	1.05	8.1

premium earned by 100 octane fuel of 2.1 cents per gallon for no full-capacity loads, 2.7 cents when 10 percent of the flights carry full-capacity load, and 7.9 cents when all loads are full-capacity.

When Bass' data in Table 2 are compared with those of Bernard, they are at least of the same order of magnitude, i.e., roughly 2 to 8 cents per gallon increased earning capacity per octane-number increase. Keith, Carey, and Ward show a value for increasing earning power of 2 cents per gallon per octane number at 100 percent load factor. Bass, and Bernard's computations are both on a basis of 100 percent load factor, and their figures for the minimum incremental earning power per octane number are in agreement with Keith, Carey, and Ward's maximum. The minimum value per octane number computed by the latter authors is 0.16 cents per gallon per octane number. It is this author's opinion that Bass is somewhat optimistic in crediting 100 octane fuel with both a 20 percent increase in specific take-off engine output and a 9½ percent reduction in specific cruising consumption. It is granted, however, that with some engines, under suitably-chosen operating conditions, increase of octane number from 87 to 100 can be expected to increase power by more than 20 percent and decrease cruising consumption by more than 9½ percent.

The data of Keith, Carey, and Ward on all up-weight, disposable load, fuel consumption, etc., for the transport used in their calculation may be used for a flight of double the length they assume. Using their figures for ratio of fuel consumptions on 100 and 87 octane fuels and for warm-up and take-off fuel weight—doubling the cruising and reserve-fuel supply and increasing the oil load by 50 percent—the payload becomes about 1100 pounds for 87 octane fuel and about 2000 pounds for 100 octane fuel. At 5.75 cents per 200 pounds passenger-mile (assumed by Keith, Carey, and Ward) the increased earning capacity of the 100 octane fuel becomes approximately 48 cents per gallon, or 3.7 cents per octane number, at 100 load factor. This last figure for earning capacity serves to emphasize the importance of fuel consumption in long-range operation.

Summarizing the findings of Bass, Barnard, and of Keith, Carey, and Ward, the increased earning power of 100 octane fuel over 87 octane fuel varies from 2 cents to $1.79 per gallon. In each of the three investigations the increase of earning power depends on a number of variables such as proportion of flights made with capacity payload, flight range in non-stop hours, and specific payload revenue. The highest premium value of $1.79 per gallon is obtained by Bass, with a specific payload revenue value of approximately 15 cents per 200 pounds passenger-mile on a 20-hour non-stop flight.

If Keith, Carey, and Ward's final estimate of 3 to 6 cents per gallon increased net earning power for 100 octane fuel over 87 octane fuel is taken in conjunction with their estimate of only 7 to 9 cents per gallon manufacturing cost of *iso*octane, it would appear certain that there is an immediate field for 100 octane fuel in existing commercial aircraft.

In the military field, the advantages of increased power, improved cruising fuel consumption, or both together, are so pronounced that cost is entirely secondary as long as potential supplies are adequate. Potential supplies of blending agents for the manufacture of 100 octane fuels[12, 13] appear to be in excess of any likely demand. In the military field the demand for performance is so intense that all possible means of improvement are taken advantage of, and none can be safely neglected. Thus with advance of engine development, a continual demand for further fuel improvement can be expected.

6. FUEL GRAVITY AND HEAT CONTENT

Fuels of 100 octane number consisting of *iso*octane and gasoline are generally uniform in gravity and heat content per unit volume. This is of importance, since modern engines are generally equipped with automatic carburetors which control the fuel supply required by the various conditions of operation by metering substantially on a volume basis. Both the aircraft and petroleum industries must face the fact that such controls cannot be effective with fuels which vary widely in heat content per unit volume. Thus, when using a blend containing 60 percent or more of aromatics, and which is equally as effective in all respects as one made with gasoline and *iso*octane, the aromatic blend will waste fuel when used with carburetor controls set for an *iso*octane blend. If the carburetor controls are set for the aromatic blend, the engine will be dangerously lean on the *iso*octane blend. In lieu of development of suitable carburetor controls for controlling fuel supply on a heat-content basis, it is to be expected that any one aircraft operator is likely to demand that his fuel supplies shall be practically uniform in heat content per gallon.

7. CONCLUSION

Aircraft operators in general have shown a regrettable tendency to consider fuel costs in terms of price per gallon. Fuel costs are a considerable item in operating cost, and the operators' reluctance to face increased gallonage cost is understandable. Cost per pound-mile of disposable or payload is, however, the real criterion of operating expense, and this may well bear no relation to cost per gallon when considering fuels of different octane numbers.

The wide differences in engine operating conditions at take-off and cruising are not usually familiar to those outside the aircraft industry. Discussion, in rather elementary terms of these phases, as influenced by fuel octane number has, therefore, been included.

It is to be expected that, following the general use of 100 octane fuels, investigation will be concentrated on the improvements available as a result of still higher anti-knock values. *Iso*paraffins of higher anti-knock value than *iso*octane are known. One of these at least appears to be in all respects a desirable aircraft fuel, and to be not impossible of commercial synthesis.

8. ACKNOWLEDGMENTS

The author is much indebted to Dr. Harold A. Beatty for critical and editorial assistance. The assistance of Mr. Val Cronstedt has been invaluable, particularly in the matter of aircraft performance.

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Fuel Systems of 1937 Automobiles

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and
R. R. COUCH†

IN the absence of information on losses from car fuel systems, it has been customary to regard systems as being adequate if they permit trouble-free operation on commercially-obtainable fuels. That this mode of classification is not entirely sound was demonstrated in the course of the Pawhuska road tests, where volumetric losses of fuel varying from 4 percent upwards, depending upon driving conditions, were determined as probable for representative cars. The tests, 251 in number, were run in a cooperative investigation conducted by the Western Petroleum Refiners Association and the Natural Gasoline Association of America.

Nine 1937 cars were driven over 10,000 miles for the threefold purpose of studying the adequacy of present fuel-system test procedures, developing new procedures, and accumulating desirable information on representative cars. Four test procedures for arriving at permissible vapor pressures were studied. Vapor-lock reference fuels of different volatility characteristics from those commonly employed were also studied in the expectation that improved duplicability and truer ratings would result through the use of more volatile reference fuels.

Results included permissible vapor pressure vs. atmospheric-temperature data on nine cars and volumetric-loss data on six cars.

Conclusions reached were as follows:

1. Since the object of vapor-lock road tests is to study and classify *fuel systems* and not fuels, it is probable that more consideration should be given to test-fuel characteristics. It would seem that more volatile reference fuels than those commonly employed might serve to indicate losses from fuel systems as well as yield the desired information as to permissible vapor pressure.

2. If sufficient care is taken and a sufficient number of tests are made, any of the road-test procedures will yield results sufficiently accurate and duplicable to be of value. The more tests that are made, the more significant the results will be.

3. Permissible vapor pressures for a range of temperatures cannot safely be predicted from a single observation.

4. Alternative methods of handling fuels in vapor-lock road tests have promise of greatly simplifying the procedure, and further thought should be given to such ideas.

5. The method for determining fuel losses, which is based on the observed differences in the densities of samples taken from the car tank and the carburetor bowl, has promise of meeting requirements for a simple loss test.

6. Losses from fuel systems, even if trouble-free operation is possible, are of sufficient magnitude to warrant attention.

7. Indications are that the over-all losses from representative fuel systems, when using the gasoline normally sold for average maximum atmospheric temperatures, will range from approximately 4 percent to some higher value, depending upon the type of driving.

8. The corresponding over-all loss in knock rating will be at least one octane number.

This paper was presented at Eighteenth Annual Meeting, American Petroleum Institute, Chicago, November 12, 1937.

I. INTRODUCTION

THE Pawhuska road tests, the results of which are dealt with in this paper, were jointly conducted by the Natural Gasoline Association of America and the Western Petroleum Refiners Association during the summer of 1937. In the course of this work 251 separate tests were run on 9 cars. The tests involved about 10,000 miles of driving over a selected course, and required three months time to complete. Although the detailed studies of the information obtained are only partly completed, the work is sufficiently far advanced to permit this preliminary report.

II. PURPOSES OF THE PAWHUSKA ROAD TESTS

The purposes of the tests will be more readily apparent after consideration has been given to the present status of the vapor-lock problem in its relationship to the fuel problem. Why this continued interest in fuels and fuel systems? In brief, the interest of the petroleum industry in car fuel-system designs is prompted by the observation that inadequate fuel systems impose restrictions on gasoline raw materials. This has been known for some time, and many papers have been given on that general subject. Besides the matter of excluding from consideration large volumes of raw materials, inadequate fuel systems also result in operating difficulties such as vapor lock, in lost mileage through losses of vaporized gasoline at various points in the system, and in quality losses such as decreased anti-knock value, decreased ease of starting, etc. These other characteristics of poor fuel systems have likewise been known for some time. Because the fuel systems of the various makes and models of cars are far from being equal in their ability to handle fuels without operating troubles and without excessive losses, fuel manufacturers have for years been constrained to observe specifications which would result in substantially trouble-free operation in the poorest systems. Entirely apart from the restrictions which such a situation imposes on fuel manufacturers, the cars which could handle a better fuel are definitely penalized. In substance, all studies to date have indicated that better fuel systems would benefit the car designers, the fuel manufacturers, and the car owners. Better systems, besides making better use of our present-day gasoline, would aid in paving the

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way toward better and cheaper fuels. In view of these known advantages, it is indeed surprising that little progress has been made in the direction of improved systems.

Why this lack of progress? Is it due to failure on the part of designers, including the "body artists," to appreciate fully this general situation? Is it due to a feeling that "merely getting under the wire" on vapor lock is sufficient? If so, isn't it possible that the lack of interest is due to lack of information on some of the effects traceable to poor design, with no methods available for obtaining that information? True, we have a number of road-testing procedures. Do such methods actually rate cars, or do they merely tell us whether a fuel would or would not give trouble-free operation? What do we know of minimum mileage losses traceable to poorly-designed fuel systems? What do we know of fuel-quality losses incurred in passing through such systems? The answer is—very little. Clearly, questions of test adequacy, true rating of systems, losses, etc., are questions which merit answers—more complete answers than we now have.

This brings us to the purpose of the Pawhuska road tests. As outlined by the steering committee in charge of this work, the purpose was a threefold one, viz.: 1, to study existing road-test procedures critically to determine their limitations; 2, to work towards the development of more satisfactory road-test procedures for the determination of permissible vapor pressures, volumetric losses, and quality losses; and, 3, to obtain as much and as complete information as possible on the fuel-system characteristics of representative 1937 cars.

III. TEST PROCEDURES

The test methods employed to obtain information on permissible vapor pressures of fuels for trouble-free operation at various atmospheric temperatures, on volumetric losses from the fuel systems, and on fuel-quality losses, will be briefly described in the following paragraphs.

A. Permissible-Vapor-Pressure Test Procedure

The procedure involved the use of one test method with three alternative types of fuel-handling equipment. In technical circles, the method is known as the 1937 tentative standard vapor-lock road-test method. In brief, it calls for test runs on the car at various atmospheric temperatures, preferably above 85° F., using products of closely-specified distillation characteristics and of different vapor pressures. For convenience, the fuel can be designated as the standard vapor-lock reference fuel. The "vapor-locking vapor pressure" is considered in this test as being the highest vapor pressure in a fuel which will permit a car to be started and accelerated to 55 miles per hour after a 5-minute stop at the end of an extended period of driving at constant speed. Samples are withdrawn from the car tank at the end of each observation of car behavior, for check purposes. It is obvious that permissible vapor pressures thus determined will be those for one of the worst conditions of operation; as, after getting under way, a car can normally handle a product of somewhat higher vapor pressure with no apparent operating difficulties. The method is inherently the soundest one for arriving at permissible vapor pressures, because the conditions are identical with those observed in normal driving. The most serious shortcoming of the method as a routine test procedure is its unwieldiness. This is due to its being a "cut-and-try" method, necessitating many trial blends and many miles of driving for a complete set of data on any one car. Alternative methods for handling the fuels in this test have been suggested as a step toward simplification. All such suggestions have been looked upon with disfavor; because, in each instance, modifications in the conventional fuel system were required, and it was feared that these would seriously affect the results. Notwithstanding past objections, three alternative methods for handling fuels were used in the course of the Pawhuska tests for the purpose of comparing results with those obtained in the conventional method. Each of these alternative methods merits a brief description.

Alternative No. 1, designated as the "rear-rack method," involved the use of a number of 1-gallon fuel containers mounted in a rack on the rear bumper of the car. A three-way valve was inserted in the regular fuel line close to the car tank in a fashion so that fuel could be used either from the car tank or from the gallon containers mounted on the rack. Fuel from the car tank would be used during the warm-up period and from the 1-gallon containers for the actual vapor-lock tests. In normal testing each container would be filled with a fuel of different vapor pressure, so that observations could be conveniently made on a range of products in any one test run. At the conclusion of each observation, a check vapor-pressure determination would be made on the remaining fuel in the container.

Alternative No. 2, designated as the "float-chamber method," involved the use of three 5-gallon containers manifolded together and mounted in the rear-seat space of the car. The feed line from these containers passed to a float chamber mounted on the rear bumper of the car on a level with the car tank. The float chamber, designed for the purpose of eliminating the effect of a static head of gasoline on the system, was of one quart capacity, and delivered directly into the car fuel system at the tank connection. In the course of testing, each of the three 5-gallon containers would be filled with a fuel of different vapor pressure. Warm-up and vapor-lock runs would be made on each tank. At the conclusion of each observation, a check vapor-pressure determination would be made on a sample of gasoline drawn from the float chamber.

Alternative No. 3, designated as the "proportioning-valve method," was identical with No. 2 except that two 5-gallon fuel tanks mounted in the rear-seat space delivered through a manually-controlled proportioning valve, and from thence to the float chamber on the rear bumper. In the normal operation of this equipment, test fuels differing from each other by 3 or 4 pounds in vapor pressure would be prepared and charged into the two 5-gallon fuel tanks. The proportioning valve, designed so that it would mix fuels accurately in increments of 5 per cent, would be set at a desired point and road-test observations made, culminating in the withdrawal of a check sample from the float chamber. By trying a number of settings in rapid order, the complete range of vapor pressures could be conveniently explored in a relatively short period of time.

The actual details of the testing procedure, methods of making observations, etc., were kept the same in each case in order to facilitate comparisons of these various alternative methods of handling test fuels.

In order to accumulate information on other possibly more suitable types of test fuels, duplicate runs

were made with a product considerably more volatile than the previously-designated standard reference fuel. This choice was prompted by the opinoin that a considerably more volatile reference fuel might afford one means of differentiating between systems which owed their fuel-handling ability to low temperatures and those which owed their fuel-handling ability to excessive wasting of vapors. The volatility characteristics of both pairs of reference fuels are shown in Figure 1. All of these fuels were prepared in quantities sufficient for the entire test program.

B. Vapor-Loss Road-Test Procedure

In the absence of a generally-accepted procedure for determining losses from fuel systems through evaporation, a new method was devised and studied. The nature of losses and the means employed by fuel-system engineers to avoid operating troubles makes the problem of loss measurement a difficult one. Obviously, any method which involves attachments to the fuel system, or which involves changes in the location, size, etc., of carburetor vents, will tend to affect losses, and will probably yield fictitious results. The soundest method would be one requiring no changes whatsoever in the fuel system. This requirement can be met by relying upon an over-all material balance of the fuel in the system. Such a procedure would require a closely-specified fuel, with provisions for drawing periodically representative samples from the car tank and the carburetor bowl.

Sampling from the car tank presented no problem. To obtain carburetor-bowl samples, a small hole was drilled and tapped in the base of the bowl sufficiently far removed from the main jet to avoid robbing the jet. An insulated copper tube of small diameter, fitted with a stopcock delivering into a chilled receiver, completed the assembly. In a series of constant-speed driving experiments, various rates of withdrawal of samples were studied. A rate was decided upon which was equivalent to between 1 and 2 per cent of the normal car consumption at that speed. Rates as much as six times greater than the standard rate of withdrawal were found to have no noticeable effect on sample characteristics.

Various methods for arriving at the material balance on the fuel were considered. After careful study the conclusion was reached that a comparison of the densities of fuel in the car tank and residual fuel in the carburetor bowl had promise of yielding the desired information. Such density values should reflect losses if the volatility characteristics of the fuel are closely specified.

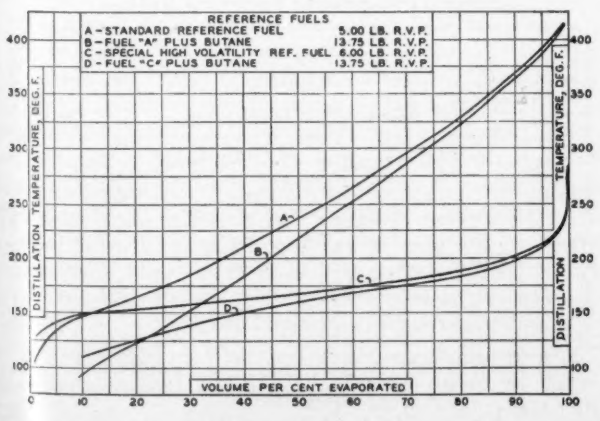

FIGURE 1
Distillation Characteristics of Test Gasolines

A series of laboratory experiments on an improvised fuel system, involving loss determinations through simple distillation and through flash vaporization, supplemented by density determinations on all products, supported this conclusion. The results were further substantiated by careful measurements on cars under test. In substance, the results indicated that each change in gravity of 1° API was accompanied by a loss of 3.5 percent by volume. The method is applicable to the measurement of losses of 10 percent or less, and indicates the minimum loss for the observed gravity change.

The normal procedure for making vapor-loss measurements consisted of sampling the contents of the car tank after the car had been thoroughly warmed up. A 90-cc. sample of residual carburetor-bowl liquid was then continuously drawn while driving a distance of 30 miles at average speed. At the conclusion of the run a second sample was taken of the fuel in the car tank. The difference between the densities of the initial and final samples in the car tank was taken as the index of tank losses. The difference between the average density of the fuel in the car tank and the carburetor-bowl sample was taken as the index of bowl losses. All densities were determined on a Westphal balance. A calibration curve of minimum loss vs. density change for the fuel used made the matter of conversion to terms of loss a simple one. The fuel used in all vapor-loss tests were the previously-designated standard vapor-lock reference fuel.

C. Octane-Number-Loss Procedure

A limited number of ASTM anti-knock determinations made on residual gasolines, prepared in the course of the laboratory studies on the vapor-loss method, indicated that vapor losses could be related to octane losses. Ten determinations made on residual samples of the 70-octane ethylized vapor-lock reference fuel indicated a loss of from 0.25 to 0.3 in octane number for each per cent loss in volume, or a loss of one octane number per degree API loss in gravity. This relationship was a consistent one for volumetric losses of 10 percent or less. No attempt was made to measure the possible effects of volumetric losses on road octane numbers, although there is some reason to believe that road octane numbers might be even more adversely affected.

IV. RESULTS

The nine cars tested included those makes of low-medium, and high-priced cars which are encountered in the largest number. All nine of the cars were examined to determine permissible vapor-pressure-temperature curves when using the standard reference fuel. Eight of these cars were also examined to determine permissible vapor-pressure-temperature curves when using the more volatile special reference fuel. Observations in the case of seven cars included, besides atmospheric temperatures, the temperature of the car tank, inlet and outlet temperatures at the fuel pump, carburetor-bowl temperature, and water-jacket, underhood, and crankcase temperatures. Six of the cars, two in the low-price bracket and four in the medium- to high-price bracket, were examined to determine volumetric losses from their

respective fuel systems. Since a detailed description of the results on each car would be time-consuming, the discussion will be confined to typical results on representative cars followed by a summary of all results.

Figure 2 shows the permissible vapor-pressure-temperature curve for car "B" when using the standard reference fuel. The corresponding curve for the considerably more volatile refrence fuel is shown in Figure 3. This particular car is one of the low-price group. The similarity in the two curves is worthwhile noting; as, apparently, the volatility of the fuels has had no influence on the results. The different fuel-handling methods employed in the tests are apparent from the designation of points. Good agreement between the various methods will be noted.

Figures 4 and 5 are similar curves for car "D." Car "D" is one of those in the higher-price bracket. Note

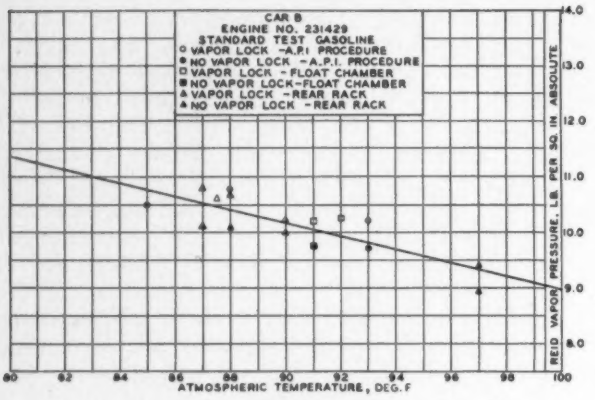
CAR B
ENGINE NO. 231429
STANDARD TEST GASOLINE
VAPOR LOCK -A.P.I. PROCEDURE
NO VAPOR LOCK -A.P.I. PROCEDURE
VAPOR LOCK - FLOAT CHAMBER
NO VAPOR LOCK-FLOAT CHAMBER
VAPOR LOCK -REAR RACK
NO VAPOR LOCK -REAR RACK
REID VAPOR PRESSURE, LB. PER SQ IN. ABSOLUTE
ATMOSPHERIC TEMPERATURE, DEG. F.

FIGURE 2

Maximum Permissible Reid Vapor Pressure (Corrected to Sea Level) as Related to Atmospheric Temperature.

the fact that in this case the permissible vapor pressures are considerably lower with the volatile test gasoline. Such differences can be laid to peculiarities in the fuel system. These results indicate that vapor-lock test results, independently determined, will be

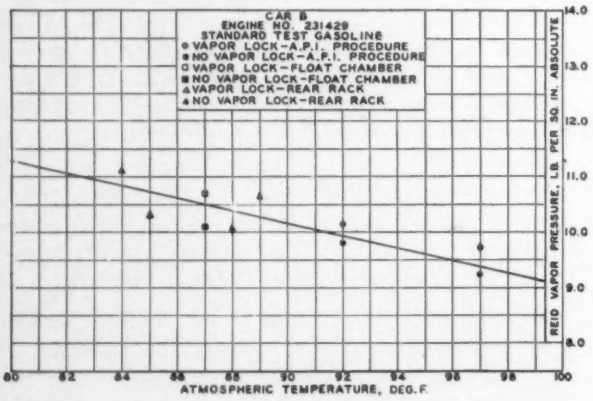

FIGURE 3

Maximum Permissible Reid Vapor Pressure (Corrected to Sea Level) as Related to Atmospheric Temperature.

virtually meaningless unless the test fuels used in the separate investigations are the same or nearly so. The more volatile reference fuel offers promise of more nearly accomplishing the desired result of sorting out fuel systems, because wastage of vapors results in lower permissible vapor pressures when fuels

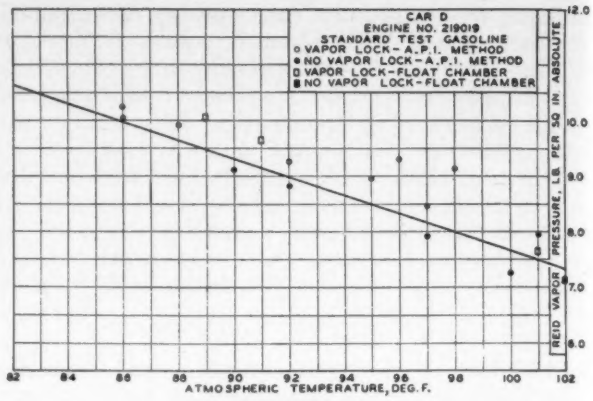

FIGURE 4

Maximum Permissaible Reid Vapor Pressure (Corrected to Seal Level) as Related to Atmospheric Temperature.

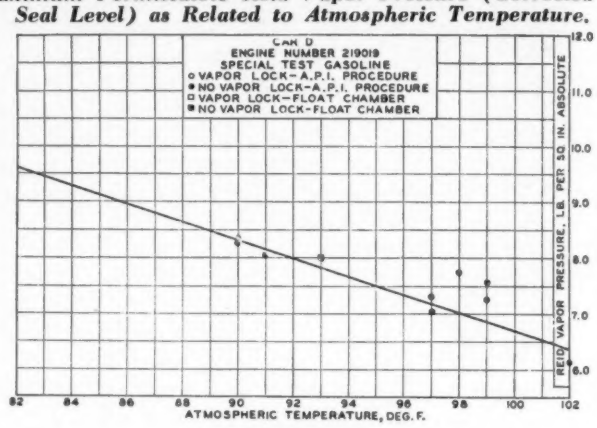

FIGURE 5

Maximum Permissible Reid Vapor Pressure (Corrected to Sea Level) as Related to Atmospheric Temperature.

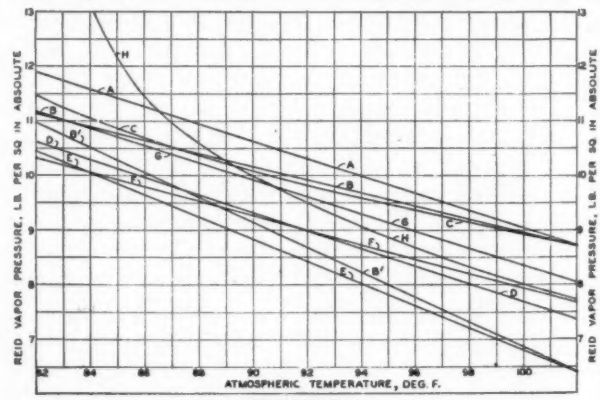

FIGURE 6

Maximum Permissible Reid Vapor Pressures (Corrected to Seal Level) for Various Atmospheric Temperatures, Standard Reference Fuel Plus Butane.

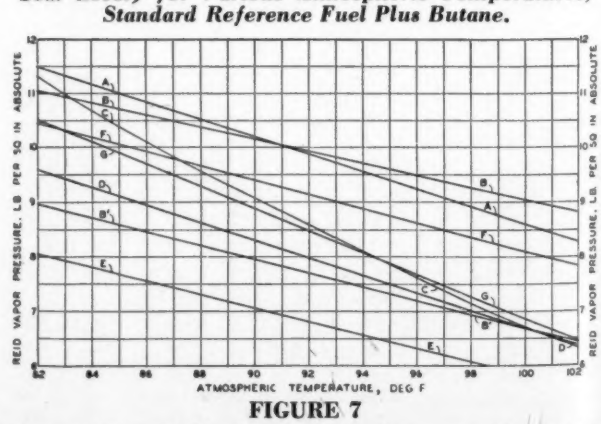

FIGURE 7

Maximum Permissible Reid Vapor Pressures (Corrected to Sea Level) for Various Atmospheric Temperatures, Special High-Volatility Reference Fuel Plus Butane.

of considerable volatility are used in the vapor-lock road tests.

Figures 6 and 7 show the permissible vapor-pressure curves for all cars tested with the two types of reference fuel. The most significant point in connection with these results is the variation in the slopes of the curves. It is obvious that the prediction of permissible vapor pressures for a range of temperatures from a single observation will be an unsound practice. To facilitate comparison, all determined permissible vapor pressures for both types of reference fuels are presented in Table 1. Table 1 includes limiting vapor pressures predicted by subtracting 1.2 pounds from the determined permissible vapor pressures for 90° F. operation. Marked discrepancies between true and predicted values will be noted.

TABLE 1
Maximum Permissible Reid Vapor Pressures as Determined for All Cars and Fuels

Car Designation	Type Reference Fuel	Atmospheric Temperature (°F.)			Predicted* Reid Vapor Pressure at 100° F.	Observed Slope or Conversion Factor
		80	90	100		
A	Standard	12.23	10.62	9.04	9.42	0.158
A	Special	11.80	10.20	8.60	9.00	0.160
B	Standard	11.38	10.15	8.96	8.95	0.119
B	Special	11.30	10.15	9.02	8.95	0.113
B′	Standard	11.42	9.10	6.82	7.90	0.228
B′	Special	9.23	7.96	6.79	6.76	0.117
C	Standard	12.00	10.12	8.92	8.92	0.120
C	Special	12.02	9.08	6.75	7.88	0.223
D	Standard	.....	9.30	7.70	8.10	0.160
D	Special	9.93	8.30	6.70	7.10	0.160
E	Standard	10.87	8.82	6.80	7.62	0.202
E	Special	8.30	7.06	5.82	5.86	0.124
F	Standard	.....	9.27	7.93	8.07	0.134
F	Special	.....	9.40	8.08	8.20	0.132
G	Standard	11.47	9.09	8.35	8.70	0.155
G	Special	10.93	8.90	6.86	7.70	0.204
H	Standard	.....	10.01	8.20	8.81	0.181

* Determined by subtracting 1.2 pound from the observed permissible vapor pressures at 90° F.

In considering all of these permissible vapor pressures, it should be kept in mind that the values are probably for a most extreme condition. Also, the vapor pressures are those determined on the car-tank contents after vapor-lock observations. They are in no wise related to or indicative of required vapor pressures of fuels at filling stations. It has been observed that cars in normal driving can handle considerably higher vapor pressures than those indicated without encountering operating difficulties.

A few brief remarks regarding the findings on the various modifications in test methods will be of interest. Each of the three alternative methods for arriving at permissible vapor pressures was found to be superior to the present tentative standard method from the standpoint of convenience and speed. As an example, the method embodying the proportioning valve was found to give results in from one-third to one-half the time normally required in the conventional method. The great saving in time required to obtain full and complete information is sufficient incentive to warrant more attention being paid to these various modifications, particularly since results were in such good agreement.

Table 2 is a condensed summary of temperature observations made on the various cars in the course of the tests. Results are given in terms of the increase in temperature above atmospheric temperature. Particularly noteworthy are the unusually-high temperature rises encountered after the 5-min. rest period.

In exploring the range of losses as influenced by temperature, vapor pressure, and type of driving, two cars representative of the lower-price bracket and one

TABLE 2
Summary of Fuel-System Temeprature Observations

Car Identification		Car "A"		Car "B"		Car "C"		Car "D"		Car "E"		Car "F"		Car "G"	
		Stabilized	After 5-Min. Stop	Stabilized	After 5-Min. Stop	Stabilized	After 5-Min. Stop	Stabilized	After 5-Min. Stop	Stabilized	After 5-Min. Stop	Stabilized	After 5-Min. Stop	Stabilized	After 5-Min. Stop
Rear tank	Average	18	4	1	0	5	16	−1	4	5	15	12	5	13	11
	Maximum	33	6	5	4	10	24	9	18	15	20	25	14	19	27
	Minimum	7	3	−4	−4	−2	9	10	−7	−8	7	2	−5	2	3
Fuel-pump inlet	Average	18	30	22	33	17	39	29	50	25	28	35	38	26	32
	Maximum	23	35	24	39	20	42	36	60	32	47	42	45	31	37
	Minimum	14	26	17	27	8	34	22	45	20	20	32	8	20	25
Fuel-pump outlet	Average	27	33	29	38	38	85	48	91	27	69	44	41	34	42
	Maximum	34	37	33	40	45	100	58	113	35	82	48	48	39	46
	Minimum	21	28	26	34	30	68	39	69	20	54	38	14	29	36
Carburetor bowl	Average	28	30	28	35	22	43	41	48	30	46	53	53	37	44
	Maximum	31	36	34	40	24	49	47	62	36	58	67	66	44	53
	Minimum	29	24	25	32	19	37	35	36	24	39	41	41	28	34
Underhood	Average	37	22	33	39	15	44	19	41	29	43	46	51	46	64
	Maximum	43	26	38	45	19	54	28	59	34	68	52	59	54	86
	Minimum	34	16	25	36	9	31	7	12	22	25	39	41	43	34
Atmospheric temperature	Average	87	87	92	92	90	90	95	95	91	91	97	97	88	88
	Maximum	89	88	97	98	96	97	106	105	100	101	104	104	96	96
	Minimum	83	83	85	86	80	80	86	86	80	80	84	86	82	82
Number of tests		4		8		9		22		16		12		11	

TABLE 3
Probable Vapor Losses for Conditions of Steady Driving at 55 Miles Per Hour—All Cars

(Losses in Terms of Volume Percent)

	Atmospheric Temperature (° F.)	Average Motor Fuel of 8.0 Lb. Reid Vapor Pressure			Average Motor Fuel of 9.0 Lb. Reid Vapor Pressure		
		Carburetor Bowl	Rear Tank	Over-all	Carburetor Bowl	Rear Tank	Over-all
Car A	90	1.02	1.40	2.42	1.52	1.66	3.18
	100	1.67	1.89	3.56	2.17	2.25	4.42
Car B	90	0.93	....	....	1.43	....	....
	100	1.55	....	....	2.05	....	....
Car C	90	0.65	....	....	1.15	....	....
	100	1.20	....	....	1.70	....	....
Car D	90	1.57	....	....	2.07	....	....
	100	2.20	....	....	2.68	....	....
Car E	90	1.00	1.30	2.30	1.55	2.30	3.85
	100	1.40	3.30	4.70	1.90	4.20	6.10
Car F	90	1.72	1.00	2.72	2.22	2.00	4.22
	100	2.33	2.70	5.03	2.80	3.70	6.50
Car G	90	1.40	1.50	2.90	1.90	1.85	3.75
	100	1.95	2.09	4.04	2.45	2.55	5.00

in the high-price bracket were selected for exhaustive experiments. Loss determinations were made in each case on the car-tank and carburetor-bowl liquids for a range of atmospheric temperatures when operating on the standard reference fuel of various vapor pressures. Observations were made both for the condition of steady driving, with the bowl sample drawn while under way, and in a few instances for conditions simulating town driving, in which case the bowl samples were drawn after a rest period of approximately one hour. The standard vapor-lock reference fuel, because of its close resemblance to our present-day average summer gasoline, was found particularly well adapted to loss studies.

In examining the loss data obtained on all cars, it was found that a reasonably good relationship existed between the vapor pressure of the fuel in the car tank, the observed carburetor-bowl temperatures for the various atmospheric temperatures, and the observed loss. This relationship is represented in Figure 8. Although admittedly not as satisfactory as actual loss measurements, this relationship does enable some predictions as to the probable losses in trip driving where only the fuel vapor pressures and the carburetor-bowl temperatures are known. Predicted losses for all cars tested on which temperature data were available gave the results shown in Table 3.

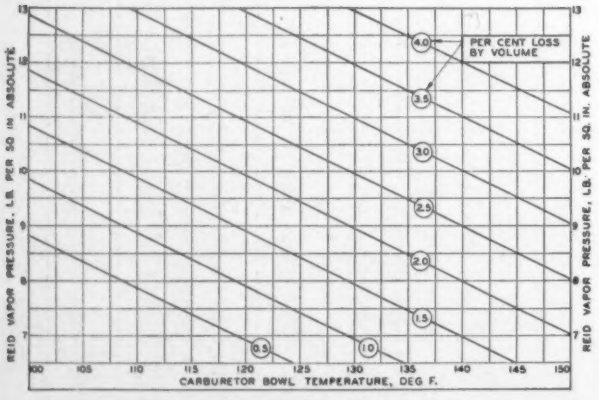

FIGURE 8
Vapor Losses from Carburetor Bowl as Related to Reid Vapor Pressure and Corburetor-Bowl Temperature.

An indication of the reliability of this method of predicting losses can be gained from Figure 9, where predicted over-all losses are compared with those actually determined. The predictions appear to be reasonably reliable.

For more complete picture on representative cars the smoothed-out normal-loss observations for two cars in the extreme-price ranges are given in Tables 4 and 5. These are the minimum losses which can be expected in trip driving, with no stops between successive fillings of the fuel tank. Observations under the more extreme conditions of town driving are not given, but indications are that they will be somewhat greater. In other words, over-all losses from the fuel system, when using the gasoline normally sold for the atmospheric temperatures indicated, will range from approximately 4 per cent to some higher value, depending upon the type of driving. These results can be readily converted to terms of octane-number loss by applying the relationship previously described in the test procedure.

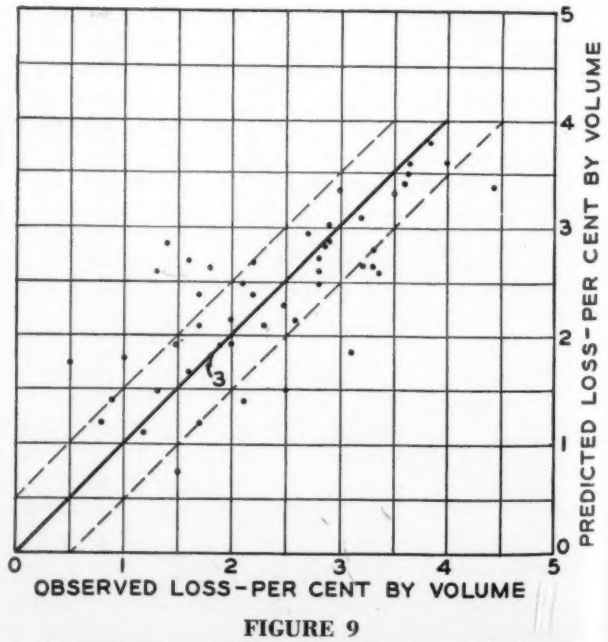

FIGURE 9
Over-all Losses—Observed Vs. Predicted Values.

TABLE 4

Predicted Vapor Losses for Conditions of Steady Driving at 55 Miles Per Hour—Car "A"

(Losses in Terms of Volume Percent)

Reid Vapor Pressure		Atmospheric Temperature (°F.)					
		80	85	90	95	100	105
7.5	Carburetor bowl	.....	.....	0.77	1.07	1.43	1.75
	Rear tank	.....	.....	1.30	1.50	1.75	
	Over-all	.....	.....	2.07	2.57	3.18	.....
8.0	Carburetor bowl	.....	0.70	1.02	1.33	1.67	2.00
	Rear tank	.....	1.18	1.40	1.66	1.89	.....
	Over-all	.....	1.88	2.42	2.99	3.56	.....
8.5	Carburetor bowl	.....	0.93	1.28	1.57	1.93	
	Rear tank	.....	1.30	1.50	1.80	1.96	
	Over-all	.....	2.23	2.78	3.37	3.89	
9.0	Carburetor bowl	0.88	1.17	1.52	1.83	2.17	
	Rear tank	1.18	1.40	1.66	1.90	2.25	
	Over-all	2.06	2.57	3.18	3.73	4.42	
9.5	Carburetor bowl	1.12	1.43	1.77	2.07		
	Rear tank	1.30	1.50	1.80	2.08		
	Over-all	2.42	2.93	3.57	4.15		
10.0	Carburetor bowl	1.35	1.67	2.02			
	Rear tank	1.40	1.66	1.93			
	Over-all	2.75	3.33	3.95			
10.5	Carburetor bowl	1.60	1.93	2.25	Vapor-		
	Rear tank	1.50	1.92	2.10			
	Over-all	3.10	3.75	4.35	Lock		
11.0	Carburetor bowl	1.85	2.17				
	Rear tank	1.66	1.95				
	Over-all	3.51	4.12		Region		
11.5	Carburetor bowl	2.10					
	Rear tank	1.83					
	Over-all	3 93					

V. CONCLUSIONS

The conclusions reached as a result of this series of road tests can be sub-divided into those dealing with the subject of test procedures and those of a more general nature.

The conclusions regarding test methods might be expressed as follows:

a. Since the object of vapor-lock road tests is to study and classify *fuel systems* and not fuels, it is probable that more consideration should be given to test-fuel characteristics. It would seem that more volatile reference fuels than those commonly employed might serve to indicate losses from fuel systems as well as yield the desired information as to permissible vapor pressure.

b. If sufficient care is taken and a sufficient number of observations are made, any of the road-test procedures will yield results sufficiently accurate and duplicable to be of value. The more tests that are made, the more significant the results will be.

c. Permissible vapor pressures for a range of temperatures cannot safely be predicted from a single observation. Actual observations must be made over the entire range of temperatures.

d. Alternative methods of handling fuels in vapor-lock road tests have promise of greatly simplifying the procedure, and further thought should be given to such ideas. It is not improbable that a simple fuel-system road-test procedure would ultimately be found as important and as useful a test as our present Reid vapor-pressure test for gasoline.

e. The method for determining fuel losses, which is based on the observed differences in the densities of samples taken from the car tank and the carburetor bowl, has promise of meeting requirements for a simple loss test.

Further conclusions of a more general nature are as follows:

1. Losses from fuel systems, even if trouble-free operation is possible, are of sufficient magnitude to warrant attention.

2. Indications are that the over-all losses from representative fuel systems, when using the gasoline normally sold for average maximum atmospheric temperatures, will range from approximately 4 per cent to some higher value, depending upon the tvpe of driving.

3. The corresponding over-all loss in knock rating will be at least one octane number.

TABLE 5

Predicted Vapor Losses for Conditions of Steady Driving at 55 Miles Per Hour—Car "G"

(Losses in Terms of Volume Percent)

Reid Vapor Pressure		Atmospheric Temperature (° F.)					
		80	85	90	95	100	105
7.0	Carburetor bowl	.....	.....	0.90	1.20	1.45	1.70
	Rear tank	.....	.....	1.25	1.46	1.77	1.70
	Over-all	.....	.....	2.15	2.66	3.22	.....
7.5	Carburetor bowl	.....	0.88	1.15	1.45	1.70	1.98
	Rear tank	.....	1.20	1.38	1.63	1.90	.....
	Over-all	.....	2.08	2.53	3.08	3.60	.....
8.0	Carburetor bowl	0.88	1.15	1.40	1.70	1.95	
	Rear tank	1.09	1.30	1.50	1.75	2.09	
	Over-all	1.97	2.45	2.90	3.45	4.04	
8.5	Carburetor bowl	1.12	1.40	1.65	1.95		
	Rear tank	1.21	1.40	1.70	1.96		
	Over-all	2.33	2.80	3.35	3.91		
9.0	Carburetor bowl	1.38	1.65	1.90	2.20		
	Rear tank	1.30	1.58	1.85	2.18		
	Over-all	2.68	3.23	3.75	4.38		
9.5	Carburetor bowl	1.62	1.88	2.15			
	Rear tank	1.45	1.75	2.04			
	Over-all	3.07	3.63	4.19	Vapor-		
10.0	Carburetor bowl	1.88	2.12				
	Rear tank	1.60	1.92		Lock		
	Over-all	3.48	4.04				
10.5	Carburetor bowl	2.12	2.38		Region		
	Rear tank	1.80	2.13				
	Over-all	3.92	4.51				
11.0	Carburetor bowl	2.38					
	Rear tank	2.00					
	Over-all	4 38					

Effect of Altitude on Anti-Knock Requirements of Cars

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A CAREFULLY-CONDUCTED test, with check readings of all data taken on a second day, was run to determine the effect of altitude on the anti-knock requirements of 12 1937 cars. Four elevations were used—approximately sea level at Sacramento, California; 6,000 feet at Hampshire Rocks on the Lincoln Highway between Emigrant Gap and Donner Pass in California; 12,100 feet near the crest of the Trail Ridge Road in the Rocky Mountain National Park, Colorado; and 5,100 feet on Highway No. 81, about 20 miles north of Denver. These locations were run in pairs; the sea level and 6,000 foot in California, and a month later the 5,100 and 12,100 foot in Colorado. This was done to eliminate the effect of changing car conditions which might have occurred during the unavoidable one-month's run of the test cars between the 6,000- and 12,000-foot elevations.

As is customary with Institute procedure for determining anti-knock requirements of cars, blends of standard reference fuels were used. The A-5 and C-10 series was used throughout its range, and was supplemented for higher octane values by blends of C-10 and F-1, and for lower octane values by blends of M-1 and A-5, and finally with *n*heptane and M-1. This is a series made up completely of straight-run fuels.

The average requirement of all cars was found to be 69 octane number at sea level, and 49 at 6,000 feet. In the second part of the test, the average requirement was 52 octane numbers at 5,100 feet, and 18 at 12,100 feet.

During the California runs a second series of fuels was used also, made up from a highly-cracked stock and blends with M-1. This series was included to show the "appreciation" or "depreciation" of cracked fuels by these cars. On the average, the car requirements with the cracked series at sea level were about two octane numbers lower than with the straight-run series—one car requiring six units lower, and several others two units lower.

At the 12,100-foot altitude the carburetor jets were changed on three of the cars, as recommended by their manufacturers for 10,000 feet. These carburetor adjustments increased the level-road acceleration of these cars from 9 to 22 percent, while increasing the anti-knock requirements only 3 to 8 units. It was obvious that the standard carburetor settings gave excessively rich mixtures at high altitudes, which caused the loss of power to be considerably more than that due to the loss of air density in the engine cylinders.

This paper was presented at Eighteenth Annual Meeting, American Petroleum Institute, Chicago, November 12, 1937.

THE object of the investigation reported here was twofold:

1. To determine the effect of altitude on the octane requirements of a typical group of 1937 cars, with:

   a. The conventional straight-run series of secondary reference fuels, and
   b. A corresponding series of cracked fuels.

2. To determine the effect of altitude on the correlation between the car and laboratory anti-knock ratings on a series of cracked fuels.

TEST COURSE LOCATIONS

The highest location in the United States at which it appeared practical to run a test car was near Fall River Pass on the Trail Ridge Road in the Rocky Mountain National Park. Here, at a section of improved highway about 20 miles from Estes Park, a fairly level section,† about one half mile long was found at an elevation of 12,100 feet. Since this location was only a few hours' drive from Denver where many level highways are available at about 5100 feet altitude, it was possible to obtain additional data at an intermediate altitude before the test cars had run enough to change their condition appreciably.

Sea-level data had been obtained about a month earlier at a location near Sacramento, California. Since it had been unavoidably necessary for the test cars to cover considerable mileage and time between the tests at Sacramento and Fall River Pass, another set of intermediate altitude runs was made during the two days following the Sacramento runs, at Hampshire Rocks, which is between Emigrant Gap and Donner Pass on Route 40. Here there was an excellent location at an altitude of 6000 feet, on an improved highway which was quite level for over a mile in length.

There were thus, in this investigation, two pairs of test runs made about one month apart; the first pair at sea level and at 6000 feet, and the second pair at 5100 feet and 12,100 feet. The two intermediate altitude tests gave an opportunity to determine if the test cars had changed appreciably in their fuel requirements during the month that had elapsed between the low- and high-altitude tests.

CARS USED

Twelve 1937 cars were used in these tests. They represented over 90 percent of all 1937 cars sold in the United States, and may be considered typical of modern cars which are kept in good condition.

These cars had covered about 14,000 miles at the time

† As required by API procedure for determinations of car anti-knock requirements.

TABLE 1
Cars Used

Cars	Per Cent of Total 1937 New Registrations*
Ford 85	22.8
Chevrolet "Master 6"	21.8
Plymouth	13.8
Dodge	7.3
Pontiac Eight	5.8
Oldsmobile Six	5.1
Buick 40	5.6
Packard 120	2.8
Chrysler Royal (C-16)	2.3
Terraplane	2.2
Studebaker President	2.1
Lincoln Zephyr	0.7
Total	92.3

* *Automotive Industries*, 77 [6] 170 (1937).

TABLE 2

ASTM Octane Number	Percent of Cracked Stock in Blend	"Sensitivity" Cracked Series
25	5.5	0
30	12.0	0
35	19.5	0
40	27.0	0
45	35	0
50	44	0
55	55	0
58	62	1.5
61	69	2.5
64	76	4
67	85	5
70	94	7
71	100	8
73	100*	8.1
76	100*	8.5
79	100*	9

*Ethyl-fluid additions of 0.20, 0.65, and 1.38 cc. per gallon, respectively.

of the first pair of tests, and 20,000 miles at the time of the second pair of tests. They had been serviced periodically by dealers handling each make of car. Despite this fact, checks made on the spark advance* of most of the cars after the tests at Hampshire Rocks and at Denver revealed that several did not have the spark setting recommended by their manufacturers.

No change was made in the spark settings found, since they were assumed to approximate what might be typical of any car of the same make as adjusted by the dealers in the territory through which it was serviced. The fact that the average car requirement at sea level was only one octane unit lower than the limit of "Q" gasoline indicates that the dealers probably set the spark to give good performance on the gasoline available, in spite of the unavoidable engine changes which result from car use, such as carbon accumulation in the combustion chamber and lime deposits in the water jackets.

TEST FUELS

A series of test fuels was made up by blending the standard ASTM-CFR secondary reference fuels A-5 and C-10 in steps differing by 3 to 5 octane numbers. When ratings were required lower than the value of the A-5 fuel (40 octane), blends were made of A-5 with the M-1 (21 octane) fuel used by the CFR Aviation Fuels Committee; and, when still lower values were required, *n*-heptane was blended with the M-1. When higher values than C-10 were required, blends were made with F-1. This entire series is thus seen to be composed of "straight-run" fuels or their equivalent. The ASTM method was used in the determination of all octane numbers.

A second series of fuels was included in the runs at Sacramento and Hampshire Rocks, which simulated cracked commercial fuels. A stabilized cracked gasoline of 71 octane was blended with M-1 for lower octane values, and additions of ethyl fluid were made for higher octane values. The use of M-1 in these blends was decided on because the very low octane value of this fuel provided blends having the largest practical content of the cracked base gasoline. Even so, the blends of lower octane number contained so little cracked stock that it was decided to drop them in the high-altitude test and the companion test at Denver. Table 2 shows the "sensitivity" of each of the cracked series of fuels, as indicated by the difference between the CFR research and ASTM anti-knock ratings. It is assumed that the straight-run series of C-10 and A-5 blends will be given the same values by both the CFR research and the ASTM methods and, therefore, have a zero "sensitivity."

Obtaining the octane requirement of each car on each of these two series of fuels was equivalent to rating individual samples of the cracked series in terms of the straight-run series as is done in rating the fuels in the laboratory on a standard ASTM-CFR engine, except at lower knock intensity. When a car requirement was not the same on both series of fuels, it was said to "depreciate" the cracked fuel if the requirement with the cracked fuel was higher than with the straight-run series. When a car rating with the cracked series was lower than with the straight-run series, the car was said to "appreciate" the fuel. This is in agreement with the colloquial terminology of the industry at present, although the terms are awkward and might be improved when nomenclature is standardized for this phenomenon.

The correlation between the cracked and straight-run gasoline series in these cars and laboratory ratings on these fuels is discussed later in this paper.

TEST METHODS

The cars were divided into two groups, each of which was tested by one of two trained knock observers on a single day. The second day, at the same location, the knock observers exchanged groups so that each car was rated independently by two observers on successive days at each location. The average of these two readings was taken as the final rating.

The test procedure, while following A.P.I. procedure for rating cars, included some additional details. It consisted of short accelerations, from 10 to 50 miles per hour, on a comparatively level road with the various test fuels, recording the maximum knock intensity, the car speed at which it occurred, and the car speed at which the knock disappeared. Two sets of curves, such as given in Figure 1, were plotted from these data: 1, car speed at which the knock disappeared, against laboratory ratings of the test fuels used; and 2, apparent knock intensity of maximum knock from each test fuel, plotted against its laboratory rating. Since fuels of three different octane ratings in each series were usually run, it was possible to extrapolate the latter curves to the octane rating which would give no knock. The former curve gave a check value, by determining the point at which the line representing the car speed for no knock coincided with the line representing the car speed for maximum knock. Further details of the test procedure are given in the appendix.

COMMENTS

1. While almost all cars showed a tendency for the knock to die out as the speed was increased, there were

* The device used for such checks was a typical commercial neon-light spark indicator. Three cars were not tested, because the device used could not be attached conveniently in the field.

four cars which showed an opposite characteristic. Cars No. 5, 6, 11, and 12 all showed a characteristic of increased knock intensity with car speed.

2. The weather condition was very uniform during this series of tests, the temperature varying from about 82 to 89°F. at all locations, except at Fall River Pass where it varied from 50 to 65°F. This lower temperature seems to be the normal effect of the high altitude, since on the same days the temperature at Denver was in the 85-90° F. range. The weather was perfectly clear during these tests, with the humidity ranging from about 30 to 40 percent.

RESULTS

Table 3 shows the individual data secured each day. Since the data on each of two consecutive days were obtained by different knock observers, it will be seen that they checked each other, in most cases, within a very few octane numbers. In those instances where

FUEL	MAXIMUM KNOCK	MAXIMUM KNOCK SPEED	KNOCK-OUT SPEED
67s	M+	25	48
73s	L+	23	37
76s	L-	20	29
70s	M-	22	44
73c	No	Knock	
70c	L-	24	32
67c	L+	22	46

Test course Sacramento

Car Plymouth

Octane requirement, straight-run 79

Octane requirement, cracked 73

FUEL	ROAD OCTANE
70c	76
67c	73

Date 7/18/37

Observer R.C.C.

Remarks

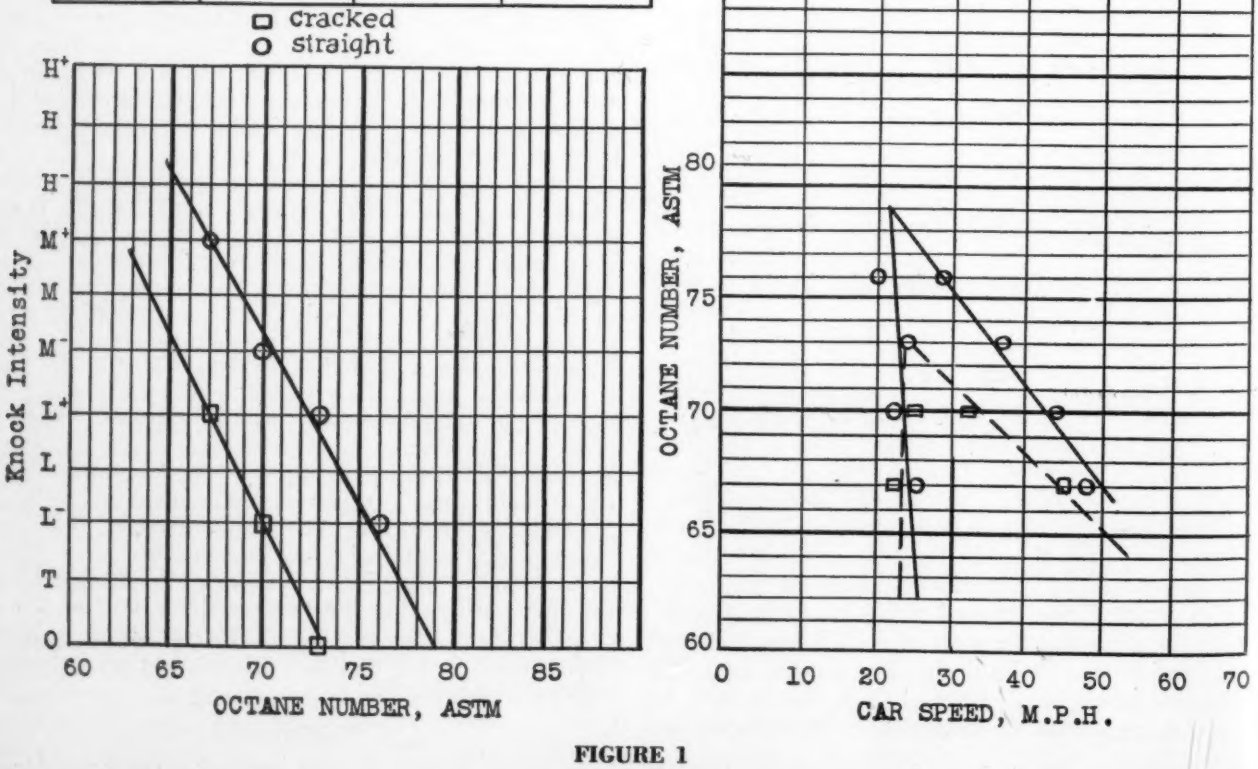

FIGURE 1
Knock Test

TABLE 3

Car No.	Altitude: Location: Date:	Straight-run Series								Cracked Series			
		Sea Level Sacramento July 1937		5,100 Ft. Denver August 1937		6,000 Ft. Hampshire Rocks July 1937		12,100 Ft. Fall River Pass August 1937		Sea Level July 1937		6,000 Ft. July 1937	
		18	19	23	24	21	22	20	21	18	19	21	22
1		79	77	66	63	62	60	26	33	73	71	59	60
2		75	79	63	67	65	64	44	44	73	76	65	65
3		73	75	57	56	53	52	26	29	70	73	58	55
4		71	67	52	55	54	49	29	24	66	67	54	47
5		61	61	44	36^{39}_{40}	40	39	−0	−0	61	60	41	42
6		61	61	57	61	38	35	25	29	61	60	40	35
7		74	..	62	61	62	63	34	38	71	..	62	61
8		68	69	53	51	52	40	0	0	69	67	54	44
9		66	66	59	55^{59}_{59}	53	55	28	25	67	66	53	55
10		64	61	42	46	35	37	0	0	66	61^{63}_{63}	36	37
11		69	63^{67}	39	40	43	39	0	0	69	64	43	44
12		66	64	49	53^{52}_{52}	40	43	15	15	68	65	41	43
Average car requirement		68.9	67.5	53.6	55.4	49.7	48.0	19	19.7	68.0	66.9	50.5	49.0

they disagreed excessively on separate days, they were able to agree with each other when making a third run. It is our belief that, in most cases, the difference found was probably a real difference resulting from mechanical changes such as could be produced by backlash or friction in the centrifugal or vacuum spark-advance mechanisms.

An evaluation of the consistency of the check readings is given by the mean deviation of the data at each location: viz., the average of the differences between the two values for each car, regardless of sign, as shown in Table 4:

TABLE 4
Mean Deviations (Octane Numbers)

Altitude:	Sea Level	5,100 Feet	6,000 Feet	12,000 Feet
Straight-run series	2.2	2.7	3.1	3.1
Cracked series	1.8	...	2.8	...

The increased deviations with altitude reflect the increased difficulties of operation at the higher locations. It is interesting to observe also that the mean deviations were less for the cracked series than for the straight-run series.

In Table 5 are shown the average data at each altitude. It will be seen that the average for all cars varied from 69 at sea level, to 52 at 5100 feet, to 49 at 6000 feet, and to 18 at 12,100 feet. There were four cars which failed to knock at 12,100 feet with unblended *n*heptane, presumably zero octane, and their requirements were accordingly rated as minus zero.

It was expected that the cars might have changed in those adjustments affecting their anti-knock requirements during the 5000 to 6000 miles run between the two pairs of tests. As mentioned previously, the reason for the Denver test at 5100 feet was to obtain a rough check on the values obtained earlier at 6000 feet. As will be shown later, the effect of altitude at 5000 feet to 6000 feet is to change the octane requirement about 3.5 units. Thus, for the 900-foot difference in altitude the octane requirements for the cars at Denver should have been about 3.0 octane higher than at Hampshire Rocks. Table 6 shows the actual differences found which, with the exception of cars 6 and 10, might be considered in as good agreement with the estimated differences as could be expected when it is recalled that the cars had been driven some 6000 miles between the tests at these two altitudes.

Even car 10 may be in line, because it showed the greatest sensitivity to altitude of any car in each of the two altitude steps from 0 feet to 6000 feet and from 5100 feet to 12,100 feet, as may be seen in Table 5.

Since the sensitivity of car 6 to each of the two alti-

TABLE 5
Straight-run Series

Car No.	Sea Level	5,100 Ft.	6,000 Ft.	12,000 Ft.	Differences: Sea Level 6,000 Ft.	Differences: 5,100 Ft. 12,100 Ft.	Differences: 5,100 Ft. 6,000 Ft.
1	78	65	61	30	17	35	4
2	77	65	64.5	44	12.5	21	0.5
3	74	57	52.5	28	21.5	29	4.5
4	69	54	52	27	17	27	2
5	61	40	39.5	0	21.5	40+	0.5
6	60	59(39)*	36.5	27(7)*	23.5	32	23.5(3)*
7	74	62	62.5	36	11.5	26	−0.5
8	68.5	52	46	0	22.5	52+	6
9	66	58	54	27	12	29	4
10	62.5	44	36	0	26.5	44+	8
11	66.5	40	41	0	25.5	40+	−1.0
12	65	51	41.5	15	24.5	36	−4.5
Average	69	52	49	18	19.6	34.2	3

*Corrected value—see last paragraph on this page.

TABLE 6

Car No.	Difference Between Car Requirement at 5,100 Ft. and 6 000 Ft. (Octane No.)
1	4.0
2	0.5
3	4.5
4	2.0
5	0.5
6	23.5
7	−0.5
8	6.0
9	4.0
10	8.0
11	−1.0
12	4.5
Average (car 6 omitted)	3

tude steps was very close to the average for all cars, it is obvious that some vital change in conditions had occurred between the two altitude steps. It was, therefore, considered justifiable to correct for this change by deducting 20 from the octane requirements of this car for both the 5100- and 12,100-foot altitude tests. With these corrections in Table 5, the average of all cars at each altitude has been plotted in Figure 2, which shows a very consistent curve. The dotted curves give the maximum and minimum values recorded at each altitude. Another curve, taken from tangents to this curve, indicates the rate of change of octane requirement at any elevation up to 12,100 feet.

MIXTURE RATIO

The lowered octane requirement at high altitudes is, of course, due primarily to the smaller weight of air drawn into the cylinders, and is similar to closing the throttle of the engine. This loss of volumetric efficiency would probably be fairly uniform for all cars at a given altitude; and it seems that, in addition to the characteristics of the individual carburetors, a reason for the differences in octane requirement shown by various cars may be the initial settings of the carburetors. With the mixture ratio set for optimum power at sea level, a car would obviously lose less power and drop less in its anti-knock requirement from the super-rich mixture at high altitude than if a car had been set with a rich mixture at sea level.

In order to learn how much difference in car performance would result in using leaner carburetor jets at high altitude, three cars were run at 12,100 feet altitude, with jets provided by the Denver dealers of the individual cars for 10,000-foot operation. In each case the car acceleration was improved, as will be seen below. The octane requirement increased also.

The change in anti-knock requirement of car 8 due to the use of the leaner jet was obviously indeterminate,

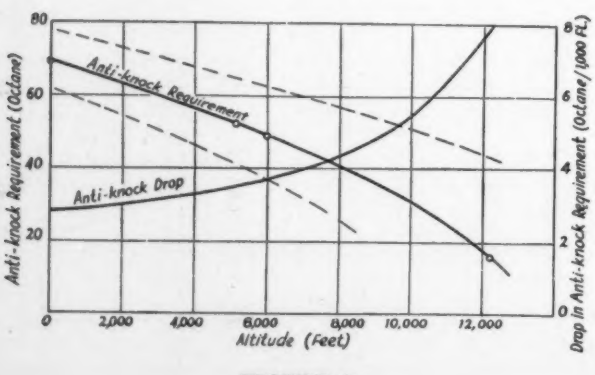

FIGURE 2

Car No.	Improved Acceleration (Percent)	Increased Anti-knock Requirement (Octane No.)
2	8.5	3
4	18.0	8
8	6.5	?

because even with the leaner jet it did not knock on the *n*heptane.

CORRELATION OF THE CRACKED-FUEL SERIES

The cracked series of fuels was matched against the straight-run series during the first pair of tests, viz., sea level and 6000 feet. They were not included in the pair of high-altitude tests, because the low anti-knock requirements necessitated blends containing so little cracked stock that their performance was expected to be almost identical with the straight-run series.

The cars are arranged in Table 5 according to their tendency to "appreciate" the cracked series of fuels. Car 1 shows a 72-octane cracked stock to be as good as a 78-octane straight-run stock (Tables 6 and 7). In other words, it "appreciates" the cracked stock 6 octane units. At the bottom of the list car 12 "depreciates" the cracked stock by 2.5 octane units. It will be seen that these cars are arranged very roughly in the order of their actual anti-knock requirements. This would be expected because the cracked series contains a larger proportion of straight-run gasoline as the anti-knock values of this series are decreased. Thus, the 65-octane blend required by car 12 contained a smaller percentage of cracked gasoline than the 78-octane blend required by car 1.

This decreasing content of cracked stock with octane number is probably just what would happen in a refinery supplying a cracked stock to the motor car trade, for it would have some cracked stock to which a low-octane straight-run stock would normally be blended in order to make up the anti-knock value required for marketing. In fact, such a series can be made only by starting with a highly-cracked stock and ending with a straight-run stock, because we are not familiar with any highly-cracked stocks which have low octane numbers and which could be used at the low end of such a series.

CONCLUSIONS

1. The anti-knock value required of gasoline by automobiles in order to suppress knock decreases with increasing altitude. For average cars, the rate of decrease varies from about 3 octane units per 1000 feet elevation from sea level, to about 7.5 units at 12,000 feet.

TABLE 7
Cracked Series

Car No.	Sea Level	6,000 Feet	Difference
1	72	60	12
2	75	65	10
3	72	57	15
4	67	51	16
5	61	42	19
6	61	38	23
7	71	62	9
8	68	49	19
9	67	54	13
10	63	37	26
11	67	44	23
12	67	42	25
Average	67.5	50.0	17.5

2. Over the large area of the Western Plains, where the altitude is over 4000 feet, average cars can use gasolines of at least 10 octane units lower value than at sea level. None of the cars tested required over 63 octane at this altitude, although some required up to 78 at sea level. As illustrated in Figure 3, there are at least 7 states which are several hundred miles from an altitude less than 2000 feet, where a gasoline can be used of about 5 octane units lower value than at sea level.

3. The mixture ratio supplied by the carburetors of average cars becomes excessively rich at high altitudes. Use of smaller carburetor jets noticeably improves the acceleration of cars under these conditions. They also increase the anti-knock requirement of the car a few units but, even so, the requirement is far below the anti-knock value of commercial gasolines.

4. The "appreciation" of the cracked series varied from 6 octane units to a "depreciation" of 1.5 units—in other words, one car gave 6 octane units higher rating to the cracked gasoline than its ASTM rating, and another car gave 1.5 units lower rating to a gasoline containing about 80 percent of a cracked stock than the ASTM method.

5. The rate of change of anti-knock requirement with altitude was only slightly less with the cracked than with the straight-run series, due to the depreciating

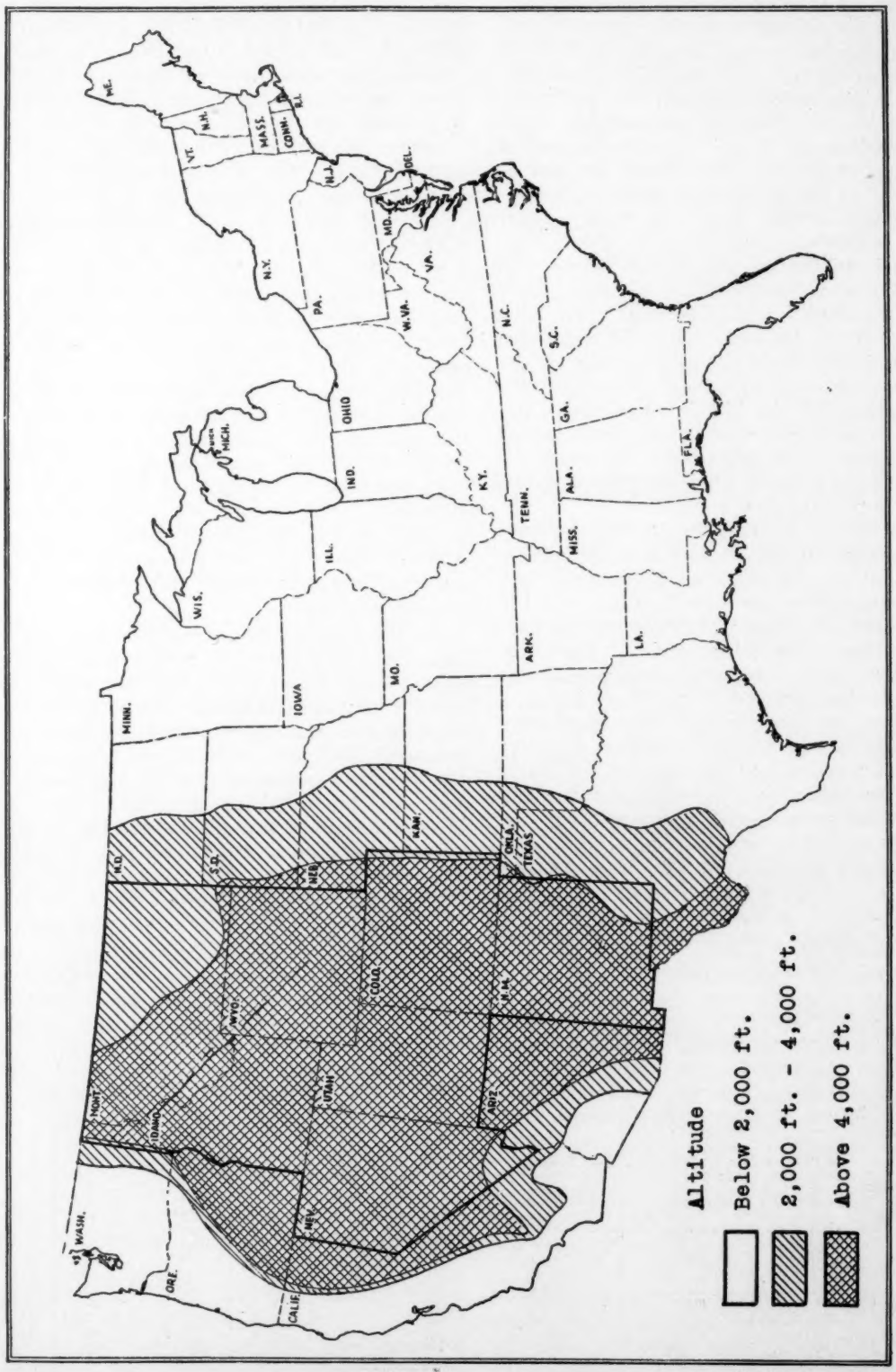

FIGURE 3
Map Showing Altitude of Western Part of the United States

effect of altitude. The anti-knock requirement obtained using the cracked series at sea level averaged 1.5 octane numbers lower than obtained with the conventional straight-run reference fuels. At 6000 feet the average anti-knock requirement with the cracked series was one unit higher than with the straight-run series.

6. The results of this test agree well with unpublished work of other organizations.

Appendix . . . Details of Test Procedure

THE care were tested in the same adjustment and conditions they had been in during the road test. The only changes necessary consisted of disconnecting the regular car fuel line at the fuel pump and installing a flexible tube which would run from the rear compartment of the car to the fuel pump. In order to expedite the test at Sacramento, two cars had fuel lines thus changed over the night before the first test and were driven to the test course drawing commercial motor gasoline from a 5-gallon can in front of the rear seat of the car. These two cars were then ready for test as soon as they arrived at the test course, and the remaining cars to be tested had their fuel lines changed over in the same order as they were to be tested.

Five gallons each of the various blends in the two series of test fuels were prepared in advance, there being 12 5-gallon standard "racing fuel pails"* available for each series of fuels. In order to avoid confusion between the two series of fuels, the pails containing the straight-run fuels were marked in red paint with the ASTM octane numbers of the blends which they contained; and the cracked series was marked with octane numbers in green paint. Throughout the test work the containers of these two series of fuels were kept at one end of the course in two separate rows.

As soon as any car was prepared for test (by changing over to the flexible fuel lead) it was taken out on the road and run for several miles while drawing commercial motor gasoline from the 5-gallon can carried in the rear compartment of the car. After a pair of cars was warmed up, they were taken over by the anti-knock observers who started out with any pail of the test gasoline which they desired to try first. When a pail of test fuel was put into the car, the can of commercial gasoline was removed and the engine was kept running on the fuel remaining in the fuel system. There was enough fuel to have the car started on the test course; and, as soon as the engine ceased firing on account of having used all available fuel, the flexible fuel line was inserted into the pail of test gasoline. Usually the inertia of the car would continue to spin the engine until it started on the test fuel.

The car was then driven along the road for at least one quarter of a mile, was slowed down to 10 miles per hour, and accelerated to a speed of 40 to 50 miles per hour by suddenly opening the throttle wide. Since the test course was approximately one mile long at each location (except at Fall River Pass) and had suitable points for the cars to turn around at each end, it was possible to have three or four acceleration readings along one trip of the course. These accelerations made it possible for knock observers to record the knock characteristics of a fuel in a car, and usually one round-trip of the car was all that was necessary on one fuel.

As the car approached the end of the test course (where all the fuels were maintained) the test driver called to the man in charge of the test fuels what the next fuel would be. The car was then turned around, and the man in charge of the fuels removed the fuel pail from the car and replaced it with the desired fuel. After a little experience it was possible for the car observer, who was sitting in the rear seat, to withdraw the line from the test fuel when the car was still far enough from the end of the course so that, after changing fuels, a very short time would be necessary to consume all the fuel remaining in the fuel lines and thus start promptly on the new fuel. In order to avoid confusion, it was customary for one of the knock observers to start on the straight-run series of fuels and for the other observer to start on the cracked series. On an average about 50 minutes were required to rate each car on both fuel series.

As the fuel supply in the 5-gallon pails became depleted, it was replenished by a man assigned exclusively to this duty. At the site where the fuels were stored, a stake truck equipped with drums of each of the four fuels required to make up the two series was located. By means of Tables 8 and 9 it was a simple matter to draw the required quantities of each base stock to make up 4000-cc. lots of fuel at a time. To make sure of no error in these blends, it was a practice to write down on a pad both the desired octane number of any blend and the

*Round heavy-gage containers with special rubber-gasket seals.

TABLE 8
Blending Proportions for Road Test Fuels
"C" SERIES

ASTM Octane No.	Percent Mixture		4,000-cc. Mixture	
	M-1	Cracked Fuel	M-1	Cracked Fuel
25	94.5	5.5	3,780	220
30	88	12	3,520	480
35	80.5	19.5	3,220	780
40	73	27	2,920	1,080
45	65	35	2,600	1,400
50	56	44	2,240	1,760
55	45	55	1,800	2,200
58	38	62	1,520	2,480
61	31	69	1,240	2,760
64	24	76	960	3,040
67	15	85	600	3,400
70	6	94	240	3,760

TABLE 9
Blending Proportions for Road Test Fuels
"S" SERIES

ASTM Octane No.	Percent Mixture			4,000-cc. Mixture		
	M-1	A-5	*n*Heptane	M-1	A-5	*n*Heptane
0	..	....	100	.....	.....	4,000
5	25	....	75	1,000	.....	3,000
10	48	....	52	1,920	.....	2,080
15	72	....	28	2,880	.....	1,120
20	95	....	5	3,800	.....	200
25	71.5	28.5	....	2,860	1,140	.....
30	46	54	....	1,840	2,160	.....
35	23	77	....	960	3,040	.....
40	2	98	....	80	3,920	.....
			C-10		*C*-10	
45	..	88	12	3,520	480	.....
50	..	74.8	25.2	2,992	1,008	.....
55	..	61.7	38.3	2,468	1,532	.....
58	..	54	46	2,160	1,840	.....
61	..	46	54	1,840	2,160	.....
64	..	38.2	61.8	1,528	2,472	.....
67	..	30.4	69.6	1,216	2,784	.....
70	..	22.5	77.5	900	3,100	.....
73	..	14.9	85.1	596	3,404	.....
76	..	7.2	92.8	288	3,712	.....

proportion of the two constituents involved. Each constituent was then drawn into separate glass graduates and blended together in a 4000-cc. graduated glass-stoppered cylinder. If there were any errors in these two measurements, this error would become evident after blending because there would not have been 4000-cc. in the mixture.

Mention should be made that the use of the "racing fuel pails" was a fortunate decision, for the usual 5-gallon square cans which were available for warming up stock, etc., proved to be unsatisfactory in some ways. In the first place, the thin flat walls of these container vibrated badly in the cars, tending to splash the fuel out of the opening. Second, several of these cans sprung leaks due to the continued vibration and the bulging of the sides resulting from the increased vapor pressure from the sun shining on the containers when sealed, and also from the decrease in atmospheric pressure when they were transferred to high altitudes. The "racing fuel pails," on the other hand, were of a more substantial gage metal and, being cylindrical, neither bulged from pressure nor vibrated from car motion. The outlet hole was much smaller and the rubber seal, together with the threaded plug which could be forced home by a suitable wrench, was quite an advantage in sealing these cans at night and opening them for the next morning's test.

Protection of the fuels from the sun was afforded at Sacramento and Hampshire Rocks by the shade of trees; but, for the high-altitude pair of tests, shade trees were not available, and a tent was improvised for the required protection.

Significance of Petroleum Research

[*Continued from page 492*]

Note should also be made of the remarkable synthesis of lubricating oils from such diverse substances as paraffin wax and natural gas, an example of molecular re-arrangement with a definite service in view.

The benefits to the public resulting from research in lubricating oil can perhaps be summarized as: 1, easier starting in cold weather; 2, lower consumption of lubricants per car-mile; 3, greater mileage from gasoline resulting from better sealing of the piston rings; 4, reduced wear on bearings and other moving parts, with resultant reduction in maintenance costs; 5, less carbon formation and, as a result, less frequent cleaning of pistons and cylinder heads.

An example of what better lubrication means may be found in the field of aviation. Superior oils produced by extraction methods, and with suitable addition agents, has increased the time of overhaul from 100 to 200, to 500 to 1000 hours, and at the same time has contributed to the smooth operation of the modern airplane engine. Because of hypoid gears with their extreme-pressure lubricants, automobile manufacturers have been able to lower the body of the car, thereby securing greater safety, reduction in weight, and material costs without important price advance in the finished car. More than that, the automobilist now enjoys relative freedom from replacing rear ends due to broken-down gears.

The use of these improved extreme-pressure lubricants in cutting oils reaches over into many manufacturing operations, for they permit greatly-accelerated production speeds in the fabrication of steels and the working of alloys hitherto impossible. Using these improved cutting oils, the average machine shop with the same personnel and equipment can turn out at least 100 percent more work.

All the time this improvement has been going on, the retail prices of the lubricants have shown no advance worth discussion. It is indeed a series of notable research and manufacturing accomplishments of direct interest to the public.

Kerosene, which to many is only reminiscent of the days of their student lamps, is still very much in the commercial picture; for it serves a worldwide market as a source of illumination and power. It required 129,930,000 barrels of 42 U. S. gallons each to meet this demand in 1936. The average annual tank-wagon price of kerosene in six representative cities of the United States for the year 1936 was $0.098 per gallon, being the lowest price since 1926, when it was $0.155 per gallon; since which time there has been a steady decline in price. In passing, one should mention the development of new types of lamps equipped with mantles and using kerosene or gasoline vapor, the result being a light of great brilliance.

Fractionation methods have led to the separation of propane and butane, which have been compressed and liquefied, and made available in the form of gas in cylinders or steel bottles, to be used wherever it has been found unprofitable to run gas mains or establish gas plants. The consumption of this liquefied gas for fuel has increased from 178,000,000 cubic feet in 1933 to 381,000,000 cubic feet in 1935. The public has had

this convenience at a reasonable price not only for use from individual containers erected outside the house, but in some cases through local distributing systems serving a very limited area. In addition, this liquefied gas fuel has been used to enrich water gas and to meet fluctuating loads. Its constant heat value and easy operation make it very convenient to handle, and assure a more uniform performance of power plants which, in turn, contribute to the comfort of the consuming public.

IMPROVED HIGHWAYS

Our highway program has profited from asphalt developments within the petroleum industry, much of the research being in cooperation with highway engineers and paving technicians. Asphalt has been found more economical in first cost, maintenance, and improvement expense than other surface materials. Notwithstanding the enviable position of the United States as compared with other countries in the matter of thousands of miles of paved roads with various surfaces, it is not likely that our paving program will ever be fully completed, because there is always the question of secondary or farm-to-market roads and the necessity of rebuilding, straightening, re-surfacing, and other factors of road improvement. The public benefits through greater comfort and ease of driving as well as through smaller repair bills and cost of upkeep for the cars. An indication of the importance of this development is found in the fact that domestic demand for petroleum asphalt has increased from 15,500,000 barrels in 1935 to 22,000,000 barrels in 1936. Nearly three fifths of this total asphalt sold in 1936 was used to surface streets and highways.

A field of the greatest importance, which has scarcely been touched, is the production of solvents and many other chemicals from petroleum as the raw material. We have known for some time of the availability in petroleum fractions of the molecules needed for this purpose, and these fractions are coming to us in an increased number and variety. Already thriving industries have been founded on such petroleum fractions —as, for example, the Carbide and Carbon Chemical Company, founded on ethylene, and the Sharples Solvent Company which has been built on the pentane fraction of natural gas. The petroleum industry itself has entered the industrial chemical field through the utilization of available hydrocarbons for the manufacture of *iso*propyl and the higher alcohols and their ethers and esters, which have been produced from olefins available in the cracked gas. Synthetic ethyl alcohol and other members of the alcohol family of important solvents are now derivatives of petroleum through the synthetic route; and the cheapness of the raw material, as well as the efficiency of the process, has made possible manufacture at lower costs in most cases than if other raw materials were used, with resulting benefits to the ultimate consumer. Indeed, by making available aliphatic hydrocarbons in large quantities, an aliphatic chemical industry has been built up which may rival in importance the aromatic chemical industry of which the products derived from coal tar is the outstanding example.

More recently, the petroleum industry has developed viscous oils and rubber-like products from gaseous hydrocarbons. These polymers have material resistance to acids, alkalis, weathering, and ageing; and may be used as coatings for all sorts of base materials. They are found useful in rubber compounds, improving the latter in many respects. There has also been made available a variety of synthetic resins made from oxidized hydrocarbons.

VARIED USE OF OILS

There are several special uses of oils to which reference should be made, for research is involved in their manufacture to exacting specifications. We refer to mineral oils used in cables and transformers, and replacement of fatty and vegetable oils in some divisions of the textile industry, and the utilization of mineral oils in the manufacture of inks. A less exacting demand comes from the development of coal-spraying to reduce dust, leaving a fuel free from odor and much easier to ignite. There should also be noted the many industrial uses of white mineral oils, varying from therapeutic uses to the preservation of eggs and apple wrappers. Low-viscosity white oils are of use in emulsions for spraying orchards and vegetables, to control insects; and in California alone in 1934 about 5,000,000 gallons of such spray were employed. White oils have also played their part in the development of mechanical refrigeration and air conditioning. A point also should be made of the extent to which especially-prepared petroleum derivatives and solvents have found their way into paint formulation, as well as in varnishes and lacquers. Petroleum thinners reached a total of 18,500,000 gallons in 1935, as compared with 3,500,000 gallons of turpentine.

The above catalogue of benefits to the public as the result of research in the petroleum industry is doubtless far from complete, and is exhaustive in no instance; but, as in all research, there are certain valuable by-products often overlooked by the public which are, notwithstanding, very real.

TAX BURDEN HEAVY

To the best of our knowledge there is no industry in the world which to the same extent has been required to carry the load inherent in its own problems and at the same time serve as a tax-collecting agency. When combined with the automotive industry, we find that the motorists pay one out of every seven tax dollars. Including state registration fees, state gasoline taxes, federal excise taxes, personal-property, city, and county taxes on automotive property and including bridge and tunnel tolls, we find an estimated total for 1936 of $1,448,266,976, of which the state gasoline tax amounts to $686,631,000. These staggering totals represent a steady climb to a new peak in 1936, which is to be exceeded by $100,000,000 in 1937 according to latest estimates.

We have had occasion in an editorial to discuss this handicap under which research labors. Much money, perhaps ten to twelve million dollars a year, is spent by the industry in furthering scientific research with a view to improved products and lower costs to the public; but, regardless of such achievements as we have related above, we cannot keep up with the tax collector. In 1936 gasoline prices in 50 representative cities averaged for the first month as follows: tank-wagon price, exclusive of tax, $0.1263; service-station price, exclusive of tax, $0.1410; state and federal gasoline tax $0.0535—giving a total, including tax, of $0.1945. Going back 10 years, we find the tank-wagon price, exclusive of tax, $0.1842; service-station price, $0.2097; total taxes, $0.0241. In a decade, therefore, the price of gasoline at the tank wagon has declined about 50 percent and the taxes have increased more than 100 percent. Going back to 1919, when the tank-wagon price was $0.2411 and the service-station price $0.2541, the total taxes were $0.0006!

From all this income—which reaches astronomical figures—since records were kept has come, among other

things, the highway, bridge, and tunnel system which, without the automobile and the petroleum industry, would never have been built. Of the total local and state mileage amounting to 3,068,921 miles in the United States, 520,351 are classified as belonging to state systems comprising roads and streets under the control of state highway departments; of those, 371,424 have been surfaced. Neither the petroleum industry nor the motorists complain over-much of the use of gasoline taxes for highway construction and maintenance; but when one sixth of state motor taxes is used for non-highway purposes, we begin to see how this so-called painless method of taxation is being employed at every opportunity to obtain funds collected at the expense of the filling station for a wide variety of unrelated purposes.

BEGINNINGS OF RESEARCH

That all this growth and development, and more, should have taken place in so few years is one of the astonishing things of our times; but it is no more so than the fact that not until 1925, only 12 years ago, did the industry as a whole begin to concern itself with fundamental research. Even the great projects of the American Petroleum Institute—with money provided by the late John D. Rockefeller and the Universal Oil Products Company—did not get under way until 1927. The industry has so often been guided in its work by specifications and requirements, and with great frequency the procedure has been to find what to add to a more or less unknown base to produce something to perform in a definite way. We cannot restrain our admiration for the long line of oil cooks who have accomplished so much. When we remember that even now we know the constituents reasonably well of but 10 percent of petroleum, we must marvel that so much has been achieved, and are left to wonder what might have been known had the petroleum industry been required to work out its salvation as did the coal-tar chemical industry. Verily, the petroleum industry seems to have been tied too closely to the automobile; and, while none can prophesy what may still be accomplished, the outsider is surprised at the lack of knowledge of the composition of the raw material, petroleum.

But uncertainty as to what might be made is certainly no bar to fundamental research. Goodyear studying rubber and trying to learn how to vulcanize it, saw only overshoes, raincoats, and other devices to protect the health of the public. He could not see automobile tires and the countless other objects of rubber which enrich the present day civilization. When Count Chardonnet looked at the silkworm on the mulberry leaf, he only dreamed of doing in the laboratory with mulberry leaves what the silkworm did; he could not see alpha cellulose from wood and the hundreds of millions of pounds of chemical fiber now produced throughout the world and used in a variety of ways. When Ernst Abbe convinced Schott of the necessity of research on glass, he was thinking of lenses for optical instruments; he would have been amazed at the thought of glass fibers now being spun and woven on textile machines and of industrial buildings composed of glass blocks. When Langmuir began his study of inert gases, he had no thought of the high efficiency electric lamp of today. And who would have prophesied that out of the research on vacua and layers of molecules would have come the radio tube? No, one cannot look at a raw material and envisage what can be made therefrom. Few inventions have been made to order. If following the Civil War surgeons had been asked to invent a better probe for finding foreign objects in the human body, it is quite likely they would have tried to better the means then employed. It is unthinkable that they would have discovered and used X-rays for the purpose.

GREAT POSSIBILITIES

There is reason to believe that in petroleum there may be found some important molecules quite different from any with which we are now acquainted, but who shall say what will be made therefrom? After all, only a small number of men have been working on fundamental research of petroleum, but what they have done has already had a stimulating effect upon those who research in the more applied problems of the industry. Dr. J. Bennett Hill has shown that, with the *Journal of the American Chemical Society* as an example, there were but two published papers in the field of petroleum in 1924, and in a single decade this increased twenty-five-fold—there being 50 such contributions in 1934. We believe it can also be shown that a sympathetic attitude toward fundamental research, and the pursuit of problems in that field, has focused much university research on this field, and has attracted better trained men to the industry. Such important personnel are naturally more at home and do better work where there is the right attitude toward research.

We feel that the industry is called upon to support the whole scheme of fundamental research. It needs no special urgence to continue adequately investigations relative to the origin and recovery of petroleum, but it should be quite sympathetic toward this other research aimed at determining the chemical constituents of petroleum and such fractions as lubricating oil. The program has in its favor the fact that fundamental research is non-competitive; the use of the results obtained through such work is a matter for individual companies, and they all profit from such knowledge in direct proportion to the competence and extent of their scientific and technical staffs. We believe it behooves the industry also to follow back along the trail and do all it can to encourage the proper training of men who may enter the industry in various scientific and technical capacities, even going so far as to insist upon, and then help to provide, if necessary, adequate faculties in institutions of higher learning.

WASTE LIMITED

Some 25 years ago a firm of consulting chemists made an exhaustive report to a lumber company indicating some possible uses for their waste material. The company was closely held and prosperous; so, notwithstanding the urging of their attorney that something be done to utilize the report, they continued for some years in the old lumber enterprise. The time came, however, when they decided to take up some of the other lines of activity. Shortly afterward there was painted on the side of the old waste burner a legend which testified to the value of the raw materials which had been burned as waste, but which would have been worth a sum truly impressive had they but begun earlier the profitable process of turning such so-called wastes into marketable products.

The case is not strictly analogous, for the physical waste in the petroleum industry has been indeed small. We now know that the burning of refinery gas as a fuel is wasteful, but it took research on polymerization to make it convincing. The use of heavy fuel oil in place of coal in large central power stations is doubtless wasteful, and research may show that the use of individual hydrocarbons, or simpler mixtures of hydrocar-

bons, than are now found in gasoline may be the wisest use of the fuel for power purposes. I predict that some day it will be demonstrated that great quantities of molecules, highly valued for unique properties, have been inefficiently used, if not indeed wasted, and that higher returns could have been obtained from what has been utilized to the best of our knowledge had we but known enough of the fundamentals underlying the amazing complex substance we call crude oil.

BENEFITS TO PUBLIC

How are we to estimate the gross over-all benefits from research applied to the petroleum industry? The very question reminds us of one of the lines in a popular song wherein we find the query: "How deep is the ocean, how high is the sky?" One could no doubt make estimates, if he were a good mathematician, to express some of these benefits in dollars and cents, but he would have totals so large as to be incomprehensible and perhaps lay himself open to the same condemnation as was given an exhibit some years ago by the Supreme Court which characterized it as "setting down figures with delusive exactness."

Earlier we have mentioned light, heat, and power as the three great services which the products of the petroleum industry promote. We have tried to indicate how research in the petroleum industry has been potent in maintaining an increasing volume of products on a descending cost curve to the public—and how, among other things, it has meant better, lighter, cheaper, and more efficient power units with longer life through better lubrication.

While the direct economic benefits of petroleum research have been passed along promptly to the public, the industry itself has profited by the resultant rapid widening of its markets, and its improving competitive position.

SOCIAL IMPLICATIONS

When we begin to think of the social implications of the benefits to the public through petroleum research, we are simply overwhelmed with the possible points for discussion. It was Kipling who asserted that "transportation is civilization," and what petroleum products have meant to transportation and to power needs scarcely be stressed here. In 1935, according to *Technological Trends and National Policy,* a report issued this year by the National Resources Committee, the maximum horsepower available in this country was approximately 1,230,816,000, of which it was estimated 965,000,000—much more than all other sources combined—was to be found in automobiles, buses, trucks, tractors, and motorcycles.

But power goes beyond mere transportation, even though that is a factor of far-reaching importance. Mobile power is actually changing our pattern of life, and giving us not villages and cities, but a new type of metropolitan existence; while concurrently the farmer has been saved from isolation. This has affected merchandising and many other elements in our economic life. The efficient, small power unit operated by gasoline, or other petroleum product, has been a most important factor in decentralizing industry. It has played its part in "an economy of abundance by increasing production and by cheapening the products of industry."

In discussing these intangible and frequently imponderable elements in the benefits to the public, we are forced to use such significant terms as comfort, convenience, safety, satisfaction, contentment, and similar terms which describe substantial progress on the part of the people in the efficient use of natural resources. Thus we move toward a scale of living enjoyed by all the people in some degree, the difference being largely that of economic income. Continually lowering prices, or even the maintenance of a reasonable price, in the face of increased demand makes even that difference less noticable. To make available these benefits to an increasing proportion of the population is perhaps the outstanding public benefit of research in the petroleum industry.

The petroleum industry owes its growth to research and the application of its results; it must continue a research program, with adequate staffs of carefully-trained and chosen men giving their attention to expertly-chosen problems, if it would maintain its position. It will join others in a sincere tribute to "Science—pilot of industry, conqueror of diseases, multiplier of the harvest, explorer of the universe, revealer of nature's laws, eternal guide to Truth."

We wish to acknowledge the invaluable assistance of a considerable number of personal friends in the petroleum industry who have given of their time to discuss with us the information presented in this paper. We shall not attempt to list their names for fear of omissions. In addition, we have consulted some of the leading publications in the petroleum field, *Automobile Facts and Figures,* 1937 edition; the reports of committees of the American Petroleum Institute; *American Petroleum Industry* (1935); and have had the privilege of examining proof sheets of *Petroleum Facts and Figures,* 1937 edition. To all these and to many others we make acknowledgment for helpful assistance, and express appreciation for wholehearted cooperation.

A Decade of Research on the Chemical Constitution of Petroleum

FREDERICK D. ROSSINI

ABSTRACT

THE PRESENT REPORT gives a review of the 10 years of research on the chemical constitution of petroleum which has been carried on since 1927 jointly by the American Petroleum Institute and the National Bureau of Standards as the API Research Project 6 in the laboratories of the latter institution at Washington. The following subjects are discussed: general method of operation; system of fractionation; methods of identification; separation of a Mid-Continent petroleum; summary of the results obtained on the naphtha fraction and the hydrocarbons isolated; results obtained on the lubricant fraction; work in progress; and future problems.

This paper was presented at the Eighteenth Annual Meeting, American Petroleum Institute, Stevens Hotel, Chicago, Ill., November 11, 1937.

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Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

THERE was completed this year a decade of work on the chemical constitution of petroleum under the program begun jointly in 1927 by the American Petroleum Institute and the National Bureau of Standards, and carried on as A.P.I. Research Project 6 in the laboratories of the National Bureau of Standards at Washington. During this period the project has contributed much new and significant information on the chemical constituents of petroleum; has devised new, and improved existing, apparatus and methods for fractionating petroleum and separating its constituents; and has developed and assembled apparatus for determining accurately the physical properties of the separated hydrocarbons. The present review of the work of A.P.I. Research Project 6 has been prepared in order to mark this 10 years of research on the constitution of petroleum, and to inform potential users of the existence and location of these data and of the conclusions which may be drawn from them.

The work on the chemical constitution of petroleum at the National Bureau of Standards was actually begun in 1926 by the late Edward W. Washburn, on a modest scale, as a project of the bureau itself. In 1927 the work attracted the interest of the sponsors of the fundamental research program of the American Petroleum Institute, and A.P.I. Research Project 6 was established. It was evident at the start that one big advantage to be gained by the merger of the resources that could be made available for this work by the American Petroleum Institute and the National Bureau of Standards was the possibility of carrying out, for the first time, a complete and unified study of the chemical constitution of one representative petroleum. Because such a comprehensive investigation had never been undertaken, the existing knowledge of the chemical constituents of petroleum, especially of molecules containing more than five carbon atoms, was relatively meager, and divergent with respect to the purposes for which the studies were made. The state of the existing knowledge in 1928 has been well summarized by Gruse.[67] Because a knowledge of the chemical constitution of its raw material is fundamental to the entire petroleum industry, such knowledge could best be ascertained in united and unduplicated effort—leaving the practical application of the data obtained to be made by the various research and development units of the industry.

Since 1928 the Institute's interest in the work carried on at the National Bureau of Standards on the chemical constitution of petroleum has been looked after by a special Advisory Committee for A.P.I. Research Project 6, acting as a subcommittee of the Institute's Committee on Fundamental Research on Composition and Properties of Petroleum, of which J. Bennett Hill is chairman and R. P. Anderson secretary. The special advisory committee for the project, which has made material contributions in shaping the direction and encouraging the progress of the work, has since its inception been headed by J. Bennett Hill. Frank W. Hall, William J. Sweeney, and Merrell R. Fenske complete the committee. Former members are Arthur E. Pew, Jr., C. O. Johns, and George M. Maverick.

In addition to the director of the project, the staff of A.P.I. Research Project 6 has been substantially as follows: to July, 1928, two research workers; to July, 1930, four research workers and four laboratory assistants; to September, 1932, six research workers and four laboratory assistants; to March, 1936, five research men and four laboratory assistants; to the present time, six research men and four laboratory assistants. As of September 1, 1937, the research staff consists of R. T. Leslie, B. J. Mair, J. D. White, F. W. Rose, Jr., A. R. Glasgow, Jr., and C. B. Willingham. Former members are M. M. Hicks-Bruun, J. H. Bruun, and S. T. Schicktanz. Until his untimely death in February, 1934, the project was actively directed by the late Edward W. Washburn, whose enthusiastic leadership and boundless knowledge served to encourage the research staff in these researches.

For this work on the chemical constitution of petroleum, the National Bureau of Standards makes available five laboratory rooms having a combined floor space of approximately 3000 square feet, and provides all ordinary supplies and certain apparatus. The project has the privilege of consulting with experts in all the various fields in which the bureau maintains an interest, and

also of utilizing the various calibration and testing services of the bureau.

II. GENERAL METHOD OF OPERATION

Two points were considered important in formulating the research program for Project 6: first, the study should be complete on one representative crude petroleum, so that the results would have a quantitative as well as a qualitative significance; second, the work should be carried out on such a quantity of the crude petroleum that, after its exhaustive separation, the fractions obtained would be substantially pure hydrocarbons in such quantity as to permit purification and accurate determination of all their important physical properties.

The general method of operation in carrying out such a study of the chemical constituents of petroleum is essentially as follows:

1. A quantity of an appropriate crude petroleum is obtained such that, after adequate fractionation, the significant constituents will each be obtained in an amount sufficient to permit purification and determination of properties.

2. The separation of the material is carried out in such a way as neither to destroy constituents already present nor to produce new ones previously absent. This requirement eliminates the use of all chemical treatment except that which is simple and carefully controlled.

3. The material is exhaustively fractionated by all the available processes into fractions which are "homogeneous" with respect to type and size of molecules. These "homogeneous" fractions are further separated by appropriate processes with the aim of obtaining substantially pure constituents. The end of the fractionation of a given portion of material is reached when, first, it is resolved into pure compounds or, second, when the portions obtained become so small as to make further fractionation impracticable.

4. When no further separation is practicable, the obtained fractions are examined with respect to their identity as pure chemical compounds, and measurements of all their important physical properties are made. When possible, a comparison of these properties with those of appropriate synthetic compounds is made in order to identify the chemical compounds isolated from petroleum.

III. SYSTEM OF FRACTIONATION

The technique of separating petroleum into its constituents which has been developed by A.P.I. Research Project 6 may be described as the systematic interlocking of the fundamental processes of fractionation and their variations.* The order in which the various methods of fractionation are used to separate a given fraction of petroleum is determined by the effectiveness of each given process in furthering the separation already attained by the preceding treatment. Thus, while a given process of fractionation may be impotent when used alone, its systematic use in appropriate combination with other processes can lead to a complete separation of an otherwise unseparable constituent.

In order to measure the degree of separation which is obtained with a given process of fractionation, and to mark the course of separation during a systematic series of fractionating operations, several indicative and conveniently measured properties are determined for the various fractions. In connection with the fractionation of the gasoline fraction of petroleum, the properties of boiling point, refractive index, and freezing point have been used as "indicators" of separation; while for the lubricant fraction the properties of refractive index, boiling point, and viscosity have been found effective for this purpose. In certain fractions, the more difficultly-measured carbon and hydrogen content or ratio may also be determined.

1. *Classification of Fractionating Processes*

The processes of fractionation employed by the project have been fundamentally the four well known operations of distillation, crystallization, extraction, and adsorption. Each of these processes has one or more variations which have been found effective in increasing the degree of separation attainable. These are as follows:

(1) Distillation.
  a. Alteration of pressure.
  b. Addition of an appropriate azeotrope-forming substance.
(2) Crystallization.
  a. Simple refrigeration with equilibrium melting.
  b. Refrigeration in an appropriate solvent.
(3) Extraction.
  a. Use of different solvents.
  b. Variation of temperature.
(4) Adsorption.
  a. Use of different adsorbents.

Every process of fractionation is based upon some physical property of the material being separated as, for example, distillation upon vapor pressure or boiling point, extraction upon solubility, and crystallization upon freezing point or melting point (and in certain cases upon solubility of the solid phase). The effectiveness of a given process of fractionation depends upon the difference in the susceptibilities of the respective constituents to the physicochemical conditions imposed by the given process. Under any given set of conditions, those molecules which have nearly the same numerical values of the "vulnerable" property which determines the separation will be the ones most difficult to separate, one from the other; while those molecules which differ appreciably in their values of the given property will be relatively easy to separate. It follows that numerical values of the given "vulnerable" property for the various fractions can be used to indicate the extent of the fractionation.

With respect to the nature of the separation attainable, the processes of fractionation may be divided according to whether they fractionate primarily with respect to size of molecule or to type of molecule. In a separation primarily with respect to size of molecules, or molecular weight, the end of a fractionation will find molecules of a given type spread among the fractions according to size or molecular weight; and, furthermore, the molecules of different types that will be found in a given fraction will be approximately of the same size or molecular weight, i.e., have about the same number of carbon atoms per molecule. In a separation primarily with respect to type of molecule, a mixture of molecules of different types, and approximately of the same size, will be resolved into fractions each containing substantially only molecules of the same type.

On this basis, the processes of fractionation may be classified as follows:

(1) Fractionation primarily with respect to size of molecules or molecular weight:
  a. Distillation at a fixed pressure.

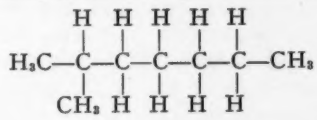
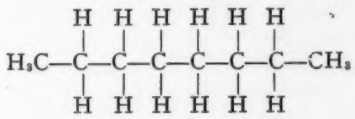
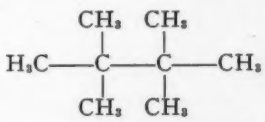
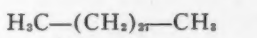
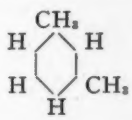
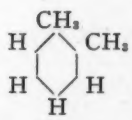
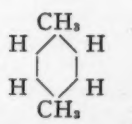
*The fundamental principles of fractionation and methods of measurement used by the project have been described many times in the literature, and no originality of such principles is implied in the present report. However, it is hoped that workers in this field may find the review helpful as a summary of such work, and that readers will refer to the research papers of the project (see p. 21) for detailed information as to the manner in which the work has been carried on, the refinements and improvements which have been made in methods and apparatus, and the references to similar previous and contemporary work (see Washburn). [1, 4, 5, 7, 29, 33]

(2) Fractionation primarily with respect to type of molecules.
   a. Extraction with solvents.
   b. Adsorption.
   c. Distillation at different pressures.
   d. Distillation on addition of an appropriate azeotrope-forming substance.

It is also possible to have a "secondary" separation with respect to size of molecules occurring in the processes of extraction and, to a lesser extent, of adsorption—provided molecules of sufficiently different size are present in the mixture being fractionated. If various types of molecules are also present, such fractionation will result in a displacement, among the various fractions, of the various types with respect to size of molecules.

In connection with separation by crystallization, it should be pointed out that while large hydrocarbon molecules usually have higher freezing points than smaller ones, the effect of the symmetry of the molecule on the freezing point is so marked that it is unsafe to draw any general conclusions. The effect of symmetry on the freezing point is well illustrated by the data given in Table 1. It is seen that normal nonacosane ($C_{29}H_{60}$) has a freezing point 40° C. below that of the highly-symmetrical hexamethylethane (C_8H_{18}). Likewise, the freezing point of paraxylene is 61° C. higher than that of its less symmetrical isomer, metaxylene.

TABLE 1
Effect of Symmetry on the Freezing Point of Several Hydrocarbons

Hydrocarbon	Empirical Formula	Structural Formula	Freezing Point (°C.)
2-Methylheptane	C_8H_{18}		—111
Normal octane	C_8H_{18}		—57
Hexamethylethane	C_8H_{18}		+104
Normal nonacosane	$C_{29}H_{60}$		+64
Metaxylene	C_8H_{10}		—48
Orthoxylene	C_8H_{10}		—25
Paraxylene	C_8H_{10}		+13

2. *Distillation*

Straight distillation at a fixed pressure is usually the best fractionating process to apply first to a crude mixture. A systematic distillation in highly efficient rectifying columns will serve to separate the material into a series of constant-boiling fractions, each of which will be a substantially pure substance, or an ideal solution of two or more compounds having practically the same boiling point, or an azeotropic mixture. The constant-boiling mixtures may then be operated on with one or more of the other fractionating tools. The degree of separation attainable by the simple process of distillation is very much greater today than it was 20 years ago, and even much greater than it was only 5 years ago. The efficiency of laboratory rectifying columns has increased to such a point that a column equivalent to 100 theoretical plates can be installed in a laboratory room of ordinary height.[14, 30, 64, 65]

Distillation at a different pressure frequently permits fractionation of a constant-boiling mixture, either an azeotropic one or one composed of two or more nearly ideal components having approximately the same normal boiling point at the original pressure, because the components of the mixture may have significantly-different values of the temperature coefficient of the vapor pressure. Because of this change in the relative partial pressures of the constituents, distillation at reduced pressure is particularly advantageous in separating two hydrocarbons of different types which have the same boiling point at atmospheric pressure. For example, a paraffin and a naphthene, each boiling at 142° C. at a pressure of 1 atmosphere, may have boiling points of about 100 and 98°C., respectively, at a pressure near 200 mm. mercury (Hg.); and a mixture of these two hydrocarbons, quite unseparable by distillation at atmospheric pressure, can be readily separated at the reduced pressure by distillation in an efficient column.[63] Such a procedure of altering the pressure was effectively employed as the "keystone" in bringing about the separation of two hydrocarbons occurring in the "methyloctane" fraction of petroleum, viz., an unidentified paraffin and an unidenti-

fied naphthene (each of nine carbon atoms) normally boiling at 140.8 and 141.2°C., respectively.[63]

Distillation in the presence of an appropriate azeotrope-forming added substance is also very effective in separating constant-boiling mixtures. If the constant-boiling mixture is already an azeotropic mixture, the added substance is one that forms a new azeotropic mixture with one of the components of the original mixture. If the constant-boiling mixture is one composed of several nearly ideal constituents having about the same boiling point, the added substance is one which forms an azeotropic mixture with one of the original components. As a matter of practical convenience, the substance added must be one that is itself readily removed, as by extraction with water, from the hydrocarbon with which it has formed the azeotropic mixture. This method of distillation with an azeotrope-forming substance has been used effectively to separate, with methyl or ethyl alcohol,[8,11] the nearly constant-boiling mixture of normal hexane and benzene; to separate certain constant-boiling mixtures of paraffin and naphthene hydrocarbons with acetic acid[50, 52]; and, most effectively, to separate, with acetic acid, the aromatic hydrocarbons from the paraffins and naphthenes, in that part of the gasoline fraction normally boiling between 154 and 162°C.[62]

Distillation at reduced pressures (between 760 and 0.0001 mm. mercury) and consequent lower temperatures, is imperative in the case of the less volatile fractions of petroleum because of their tendency to decompose when heated for long periods of time at their normal boiling temperatures. For such material, the available range of pressures for distillation becomes correspondingly limited. Several types of apparatus for distilling the lubricant fractions of petroleum under high vacuum have been used by the project.[1, 43, 100]

3. *Crystallization*

Crystallization by simple refrigeration is especially useful in separating a component which is present in large amount (such as a normal paraffin previously concentrated by distillation) from a mixture which crystallizes on cooling. A convenient and effective method to use in this case is that of equilibrium melting: the entire cut is first solidified and thoroughly mixed (as a slush) to secure homogeneity; and then, as the temperature is raised, most of the impurities are centrifuged off as a liquid from the more or less pure crystals of the wanted hydrocarbon. Repeated fractionation in this manner produces hydrocarbons of extremely high purity. This method of fractionation has been a most important one in the work of the project, and several types of apparatus have been described.[10, 18]

The method of crystallization from a solvent is used when the given mixture contains no one hydrocarbon in large amount, and when the fluidity is so low that the mixture solidifies to a glass on cooling. To provide for the crystallization of the wanted component, its mobility in the liquid state is increased by dissolving it in a suitable liquid solvent. The solvent must be one that remains fluid at the operating temperatures, and that is easily removed—as by simple evaporation—from the hydrocarbon mixture. Several types of apparatus for this method of fractionation have been devised by the project, using as solvents methane, ethane, propane, ethylene, dichlorodifluoromethane, dimethyl ether, and ethylene chloride.[26, 32, 36, 43]

4. *Extraction*

Fractionation by extraction is accomplished by using an appropriate liquid solvent in which the constituents of the given mixture will distribute themselves in proportions differing from those which they had in the original mixture. Several types of laboratory extraction apparatus have been developed by the project, for fractionating both the gasoline and the lubricant fractions of petroleum;* and included among the solvents used for this purpose are sulfur dioxide, aniline, acetic acid, acetone, and methyl cyanide.[11, 19, 43, 48, 59, 73]

5. *Adsorption*

By means of adsorption with silica gel, it has been found possible to remove effectively the aromatic hydrocarbons from a mixture of these with paraffin and naphthene hydrocarbons. Although the capacity of the gel is small, the removal of the aromatic constituents can be made practically complete. Adsorption with silica gel also effects a small but significant separation of naphthenes from paraffin hydrocarbons. A simple type of apparatus has been devised for these fractionations.[40]

6. *Controlled Chemical Treatment*

It sometimes happens that it is difficult to effect the final purification of a given hydrocarbon by purely physical means; and, in this case, carefully-controlled chemical treatment may serve to remove the last impurities. An example of this is the use of chlorosulfonic acid to prepare "best" samples of the lower-boiling normal paraffins.[17, 66]

If two isomers having boiling points very near to each other are present together in a final fraction in amounts which nearly correspond to the composition of their eutectic mixture, separation by distillation and crystallization will be extremely difficult. In this case the separation may be effected by chemical treatment if there is found a simple chemical reaction or reactions which will preferentially remove one of the constituents. An example of this is the use of sulfonation, with subsequent hydrolysis at an appropriate temperature to recover the hydrocarbon, to separate metaxylene from paraxylene, ethylbenzene from the xylenes, and mesitylene from pseudocumene.[23, 27, 32]

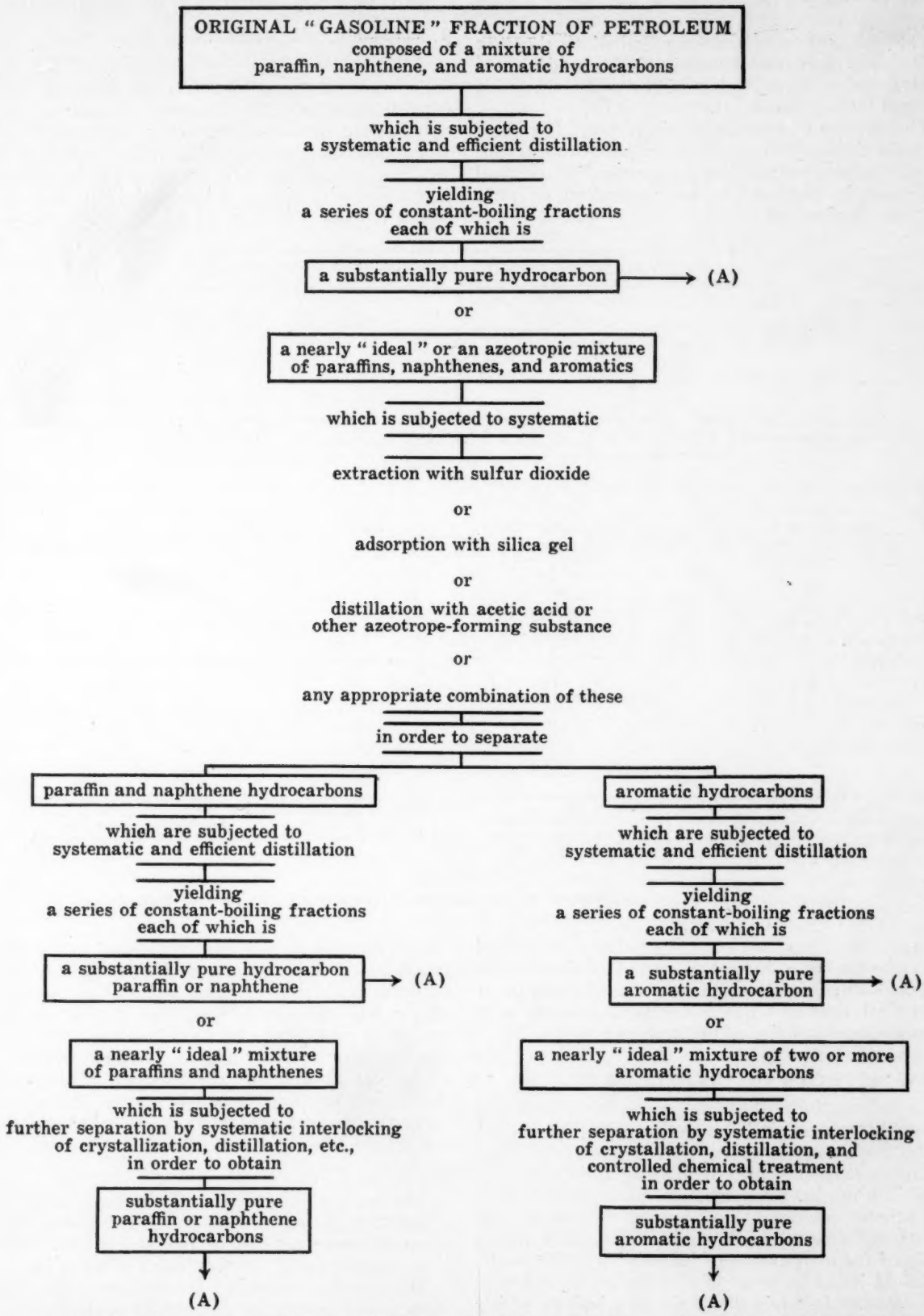
In some of the earlier work the aromatic hydrocarbons benzene and toluene were removed from their mixtures with paraffin and naphthene hydrocarbons by carefully-controlled nitration to form 1,3-dinitrobenzene and 2,4-dinitrotoluene, respectively. However, such separations can now be carried out effectively by the purely physical methods recently developed for separating aromatic hydrocarbons from paraffins and naphthenes by adsorption with silica gel[40] or by distillation with acetic acid.[52, 62]

7. *Schematic Outline of the System of Fractionation*

In Figure 1 is given a schematic outline of the manner in which the foregoing principles and processes are applied in the systematic fractionation of the gasoline or kerosine fractions of a given crude petroleum in order to separate the material into its significant constituents. The same general method would also be applicable to any narrower cut of petroleum in this range of volatility. Much of the success of a given separation depends upon the judicious selection of the order in which the appropriate processes of fractionation are carried out. It can be said, in general, that in separating pure hydrocarbons from the gasoline fraction of petroleum the normal paraffins are least difficult, the aromatics next, with the branched-chain paraffins and the naphthenes being the most difficult to separate.

In connection with the separation of the lubricant fraction into its significant constituents, or into final fractions which are homogeneous with respect to size

* See also Cannon and Fenske.[107]



(A) Subjected to further purification by distillation, crystallization, adsorption, extraction, carefully-controlled chemical treatment, or any appropriate combination of these, in order to obtain the final pure hydrocarbon.

FIGURE 1

Schematic Outline Illustrating the Separation of the Gasoline Fraction of Petroleum.

and type of molecules, the procedure is in general similar to that employed for the volatile fractions as given above. However, the work of separating the lubricant fraction is very much more difficult for the following reasons:

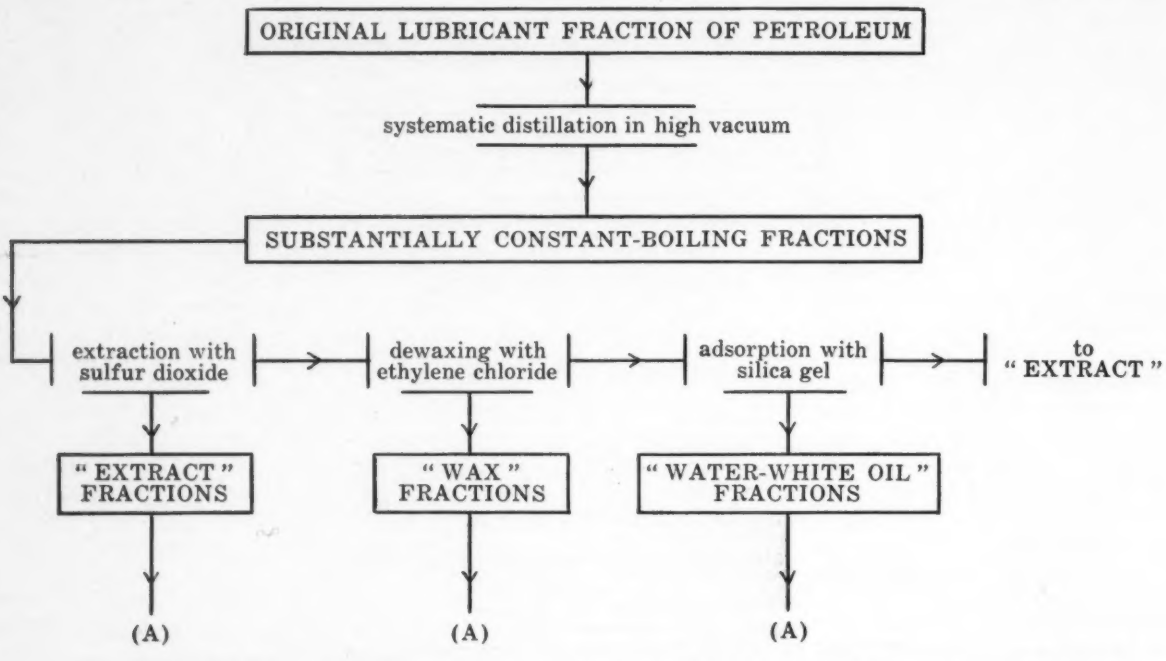
(a) The distilling processes are limited to those at exceedingly low pressures because of the tendency of hydrocarbons of high molecular weight to decompose at their normal boiling temperatures.

(b) The number of constituents is very much greater than in the fractions of low molecular weight and, consequently, a correspondingly larger quantity of original material must be obtained if the separation of pure hydrocarbons is aimed at.

ate physicochemical properties may be made, and the results correlated with the properties of pure hydrocarbons of known structure in order to ascertain the type of molecule contained in the given fractions.

1. *Important Physicochemical Properties*

The physicochemical properties which are considered important by the project for purposes of record and identification are the following: boiling point (at an appropriate pressure), freezing point, density, refractive index, molecular weight, carbon and hydrogen composition, critical solution temperature in aniline or aniline point, viscosity, and infrared (1 to 2 μ) absorption spectrum. In addition to these properties—most of



(A) Subjected to a second systematic distillation in high vacuum in order to separate the material according to size of molecules or molecular weight. Following this, each of the substantially constant-boiling fractions is subjected to an extended interlocking separation by extraction, crystallization, adsorption, and distillation, in appropriate combination, in order to obtain "homogeneous" cuts containing molecules of substantially similar size and type, and, if sufficient material is available, to obtain pure hydrocarbons of high molecular weight.

FIGURE 2

Schematic Outline of the Method of Separating the Lubricant Fraction of Petroleum.

In Figure 2 is shown a schematic outline of a method which may be employed in separating the lubricant fraction of petroleum into its significant constituents, or at least into final fractions which are homogeneous with respect to the type and size of molecules.[43, 48]

IV. METHODS OF IDENTIFICATION

After a substantially pure compound has been separated from petroleum, it becomes necessary to record all of the important properties of a purified "best" sample and, where possible, to identify the compound by comparison of these properties with those of appropriate synthetic compounds of known structure. The number of different physicochemical properties which are employed for the purpose of identifying a given substance should be as large as is practicable, in order to leave no reasonable doubt as to the conclusions which may be drawn. Washburn[5] has discussed the necessary criteria which must be satisfied in determining whether a given fraction is a pure substance.

In those cases where, because of the lack of material, the separation is forced to stop at the stage of "homogeneous" fractions containing molecules of about the same size and type, measurements of all the appropriate which, but usually not all, are determined on all the final fractions—it is sometimes desirable to determine values of the refractive dispersion and optical rotation, and to obtain photomicrographs of the crystals. As time goes on, there will likely be added to the above list other characteristic properties, including surface tension, ultraviolet absorption, far infrared absorption, X-ray diffraction patterns, heat of fusion, etc., as these become readily and accurately measurable and significant for identification of structure.

2. *Boiling Point*

The boiling point is one of the most commonly used properties of organic liquids. In general, the boiling point increases with molecular weight, for a given type of compound; and, for the three classes of hydrocarbons in the gasoline fraction of petroleum—paraffins, naphthenes, and aromatics—molecules with about the same number (± 1) of carbon atoms will usually be found in the same boiling range. For a pure substance, the accurate determination of the boiling point requires that there be thermodynamic equilibrium between the liquid and vapor; that the thermometer be at the same temperature as the liquid and vapor; and that the pressure at the place where the temperature is determined

be accurately known. For the most accurate determinations of the boiling points, a platinum resistance thermometer is used, together with an apparatus having a boiler of the Cottrell, Washburn, or Swietoslawski type.[8, 22, 97, 98, 99, 102] Apparatus of special type is required to determine the boiling points of hydrocarbons of high molecular weight at low pressures (near 1 mm. mercury).[38]

3. *Freezing Point*

The freezing point is an important property for the identification of a substantially pure substance because of its uniqueness in having no uniform variation with type or with size of molecules. While the freezing point may, under certain conditions, be said to increase with molecular weight, the influence of the symmetry of the molecule on the freezing point is so marked as to prevent any broad generalizations along these lines being made, except for molecules of the same type and degree of symmetry(see the data in Table 1).

In determining the freezing point experimentally, care must be exercised to obtain equilibrium between crystals and liquid; and an accurate thermometer, preferably a platinum resistance one, should be used. For an absolutely pure substance, the time-temperature curve obtained in the freezing experiment will be horizontal at constant temperature during the time the two phases are in thermodynamic equilibrium. If the substance contains some impurity which is soluble in the liquid and insoluble in the solid, the initial freezing point will be depressed, and the slope of the "flat" will be increased, by an amount roughly proportional to the amount of impurity. If the heat of fusion of the substance is known, the difference between the initial freezing point and the temperature at which a known fraction of the material is frozen can be utilized to estimate the amount of liquid-soluble and solid-insoluble impurity in the sample.[68, 105] If the material is a mixture of constituents in amounts corresponding to the composition of the eutectic, the time-temperature curve will show a perfect "flat" for the duration of the freezing time; but the substance will not, except as an extremely remote possibility, be an exactly constant-boiling one.[97, 98]

The apparatus and procedure used by the project for determining freezing points and freezing curves are simple but effective.[8, 22]

4. *Density and Refractive Index*

The properties of density and refractive index are important ones, because they are characteristic of the type of molecule and can be measured easily with standard apparatus. The values of both density and refractive index increase in the order paraffin, naphthene, and aromatic; and, for molecules with 8 or 9 carbon atoms, have the following approximate values, respectively: density, 0.71, 0.77, 0.87; refractive index, 1.40, 1.425, 1.50.

Important properties involving both the refractive index and the density are the specific refraction and the specific dispersion, the latter property being the difference in the specific refraction for two given wave lengths of light. Each of these properties is characteristic of the different types of molecules and of their content of paraffin, naphthene, aromatic, and olefinic groups.[77, 88] For molecules with about 24 carbon atoms, the Lorenz-Lorenz specific refraction,* calculated for the D line, $\frac{1}{d}\left(\frac{n_D^2-1}{n_D^2+2}\right)$ has the following approximate values: one-ring aromatics, 0.3313; paraffins, 0.3345; naphthenes, 0.3345—(0.0045) (number of rings). In this case, each naphthene ring produces a substantially constant decrease of about 0.0045 in the specific refraction. On the other hand, for the same molecules, the Lorenz-Lorenz specific dispersion, calculated for the G' and C lines,

$$\frac{1}{d}\left[\frac{(n_{G'}^2-1)}{(n_{G'}^2+2)}-\frac{(n_C^2-1)}{(n_C^2+2)}\right]$$

has the following approximate values: one-ring aromatics, 0.0150; paraffins, 0.0081_8; naphthenes, 0.0081_8—(0.0001_3) (number of rings). In this case, each naphthene ring produces a substantially constant decrease of about 0.0001_3 in the specific dispersion.

As is pointed out later, the properties of refractive index and density, and various combinations of them,[77, 88, 95] are especially useful in classifying hydrocarbons broadly according to type and, in some cases, even in distinguishing between various possible isomers.[69]

5. *Critical Solution Temperature in Aniline and Aniline Point*

The critical solution temperature in aniline is another property which is broadly a function of the type of molecule, although for each class of hydrocarbons there is usually a gradual increase in its value with an increase in the number of carbon atoms in the molecule. In this connection, there should be distinguished the critical solution temperature in aniline, which is the maximum temperature (of all compositions) at which two phases coexist, from the usually not greatly different aniline point, which is the maximum temperature at which two phases coexist for the special composition of 50 percent by volume each of oil and aniline. The critical solution temperature in aniline increases in the order aromatic, naphthene, and paraffin; and, for molecules with about eight carbon atoms, has the following approximate values, respectively: —20, 45, and 70°C.

6. *Molecular Weight*

A knowledge of the molecular weight and of the carbon and hydrogen content of a given hydrocarbon is indispensable for record and identification. Combination of the values of these two prperties with the atomic weights of carbon and hydrogen permits calculation of the molecular formula, C_nH_{2n+x}.

For determining the molecular weights of volatile hydrocarbons, the project has used variously a modified Victor-Meyer apparatus[6] and the method of freezing-point depression.[36] For determining the molecular weights of non-volatile fractions, an accurate differential ebullioscopic apparatus, involving determination of the boiling-point elevation of an appropriate solvent, has been developed.[37]

7. *Carbon and Hydrogen Content*

The determination of the carbon and hydrogen content is made by burning the hydrocarbon in an atmosphere of oxygen and collecting the water and the carbon dioxide produced in weighed absorption tubes. Given the molecular weight,[7] the ratio of the mass of water to the mass of carbon dioxide produced in the combustion must be determined accurately in order to obtain a precise knowledge of the value of x in the formula C_nH_{2n+x}.

With the apparatus which has been developed at the National Bureau of Standards [1, 70, 71, 72] it is possible to determine, for gaseous, volatile and non-volatile liquid, and solid hydrocarbons, the ratio of the mass of water to the mass of carbon dioxide produced in the combustion, with an uncertainty ranging in various cases from 2 to 5 parts in 10,000. For a pure hydrocarbon that contains about 14 percent by weight of hydrogen, an uncertainty of 5 parts in 10,000 in the ratio of the mass

* In these formulas, n is the refractive index for the given wave length and d is the density. For the D, G', and C lines, λ=5,893, 4,341, and 6,563 A, respectively (see Waterman et al., [77, 88] and also Mair and Willingham[42]).

of water to the mass of carbon dioxide corresponds to an uncertainty of about ± 0.007 percent by weight of hydrogen, or to an uncertainty in the value of x (in the formula C_nH_{2n+x}) of ± 0.007 and ± 0.03 for molecules of 7 and 30 carbon atoms, respectively.

In order to obtain such a high accuracy, it is necessary to have glass-to-glass connections,[1] to follow a careful procedure in preparing and manipulating the absorption tubes, and to make certain important corrections to the observed increases in weight.[70, 71] These latter corrections can be made less important by weighing the tubes always filled with hydrogen gas.[70] In determining the water and carbon dioxide, two absorption tubes are used in series—the first containing anhydrous, or slightly hydrated, magnesium perchlorate to absorb the water; and the second containing "Ascarite," a prepared mixture of sodium hydroxide and asbestos, to absorb the carbon dioxide. Both tubes contain at the exit end phosphorous pentoxide, and the gases entering the reaction zone are purified with the same reagents in the order "Ascarite," magnesium perchlorate, and phosphorous pentoxide—the oxygen to be used for combustion being first passed through a pre-heater for removing combustible material.

If the material being analyzed contains sulfur and nitrogen, as in the case of the "sulfur-dioxide-soluble" portion of the lubricant fraction, special reagents and precautions are employed to remove the oxides of sulfur and nitrogen from the products of combustion before they enter the absorption tubes[73]

8. *Infrared Absorption Spectra*

The infrared absorption spectra have been recorded in the region of wave lengths from about 1 to 2μ (actually 11,200 to 18,500 A or 8,900 to 5,400 cm^{-1}), where the *C-H* vibrations are active, for all the hydrocarbons which have been separated from petroleum by the project, and for a number of other pure hydrocarbons. Altogether, the project has now recorded, through the material cooperation of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, the infrared absorption in the regions 5400 to 8900 cm^{-1} for 55 different hydrocarbons, including paraffins, naphthenes, and aromatics, ranging in size from 5 to 36 carbon atoms per molecule.[28, 54]

Until this year these infrared data were used only as "fingerprints" for record and, in a qualitative way, to make a number of distinctions between the spectra of different types of molecules. In order to make this property more effective and useful, the project has recently completed a quantitative analysis, with respect to the component structural groups, $—CH_3$, $>CH_2$ $\rightarrow$ CH, and >CH (aromatic), of the infrared molal absorptive indices for these 55 hydrocarbons in the given regions of wave length.[57] From the data on the known hydrocarbons, values of the absorption coefficient for the various individual structural groups at appropriate wave lengths have been calculated. Combination of these values with the molal absorption actually measured at the given wave lengths for an unknown hydrocarbon permits calculation of the number, n_a, n_b, n_c, and n_d, respectively, of $—CH_3$ $>CH_2$ $\rightarrow$ CH, and > CH (aromatic) groups in the unknown hydrocarbon. Since the molecular weight and the carbon and hydrogen content of the unknown hydrocarbon permit one to compute its molecular formula, C_nH_{2n+x}, the values so found for n_a, n_b, n_c, and n_d must further satisfy the following conditions:

$$n_a+n_b+n_c+n_d>n \quad (1)$$

$$3n_a+2n_b+n_c+n_d=2n+x \quad (2)$$

The fact that the sum of n_a, n_b, n_c, and n_d, may sometimes be less than n (the total number of carbon atoms in the molecule) is due to the possibility of there being in the molecule one or more carbon atoms.

In applying this method of analysis to the determination of the number and kind of structural groups in an unknown hydrocarbon, the following procedure is used[57]:

(a) Measurement is made of the transmission of the unknown hydrocarbon in solution in carbon tetrachloride, for the regions of wave length 5400 to 7400 cm^{-1} and 7900 to 8900 cm^{-1}, with the concentration of the hydrocarbon so adjusted as to give a transmission of from 40 to 60 percent in the given region.[28]

(b) The transmission curves so obtained experimentally are reduced to curves of the molal absorptive index, using the relation:

$$k=\left(\frac{1}{cd}\right) log\left(\frac{I_o}{I}\right)$$

where: I_o and I are, respectively, the intensities of the incident and transmitted light; c is the concentration of the hydrocarbon in moles per liter of solution; d is the length in centimeters of the cell through which the light passes; and k is defined as the molal absorptive index.[28]

(c) For the given wave lengths selected for determining the various structural groups, values of the molal absorptive index are recorded for the unknown hydrocarbon.

(d) Combination of these experimental values of k with the values of the unit coefficients of absorption for the various groups at the appropriate wave lengths yields a series of simultaneous equations of the form:

$$k=n_aA+n_bB+n_cC+n_dD \quad (4)$$

where: k, A, B, C, and D, are known and n_a, n_b, n_c, and n_d are to be determined.

(e) The given simultaneous equations are solved for n_a, n_b n_c, *and* n_d, respectively, the number of $—CH_3$, $> CH_2$, $\rightarrow$ CH and > CH (aromatic) groups in the unknown molecule, and to each value an estimated uncertainty is assigned

(f) The values obtained for n_a n_b, n_c, n_d are correlated with the molecular formula, C_nH_{2n+x}, according to the above equations (1) and (2).

From present indications, it appears that the above method of analysis will prove to be extremely useful in the elucidation of the component structural groups of paraffin, naphthene, and aromatic hydrocarbons which cannot be identified on the basis of the other physicochemical properties because of the lack of data on appropriate synthetic hydrocarbons of known structure.

9. *Photomicrographs of Crystals*

An apparatus was developed for taking photomicrographs of crystals of hydrocarbons at low temperatures, and such photographs were obtained of crystals of various final fractions separated from that portion of petroleum normally boiling between 115 and 124 deg. C., and of 28 known pure hydrocarbons (9 aromatics, 6 naphthenes, and 13 paraffins).[47, 53] From these studies it is concluded that condensed molecules tend to form nearly equidimensional polyhedrons while open-chain molecules tend to form elongated prisms; that molecules containing both condensed groups and open chains tend to form crystals of intermediate structure; that successive members of the series of normal paraffins cannot be distinguished by the appearance of their crystals; and that hydrocarbons of different types may sometimes bear a superficial resemblance.[53] The appearance of the crystal forms as shown by photomicrographs of crystals can

be utilized in conjunction with other properties to identify the main constituents in mixtures of hydrocarbons.

10. *Use of Physicochemical Properties in Characterizing Mixtures of Hydrocarbons*

In any discussion of the use of physicochemical properties for record and identification, it is important to point out the use of such properties in broadly classifying a more or less closely fractionated cut of petroleum. For such correlation, a number of functions or combinations involving two or more properties have been developed by various investigators, and these methods have been strikingly successful in characterizing a mixture of petroleum hydrocarbons with respect to their "average" chemical constitution or the "predominating" constituents. Some of the combinations of properties used in this manner are: viscosity and density[74, 84]; molecular volume and molecular weight[75]; refractive index and molecular weight [76]; viscosity and temperature [78, 79, 80]; density and boiling point[81, 82]; viscosity and boiling point[83]; molecular volume and surface tension[85, 86]; refractive dispersion and molecular weight[88]; aniline point and density or molecular weight[89, 90, 91, 92, 93, 94]; refractive index and density[95]; specific refraction and molecular weight.[77]

Use of some of the above functions has been made by the project in connection with the determination of the chemical constituents of "homogeneous" fractions of "water-white" oil separated from the lubricant fraction of petroleum.[49]

V. PROCEDURE FOLLOWED IN SEPARATING A MID-CONTINENT PETROLEUM

As pointed out in the introduction of this paper, the work of the project was to be carried on systematically on one representative crude petroleum, whose composition would be expected to lie between the extremes of Pennsylvania crude on the one hand and California or Gulf Coast crudes on the other. Accordingly there was obtained, through the courtesy of Marland Oil Company (now part of Continental Oil Company) a large uncontaminated sample of a Mid-Continent crude from well No. 6 of the South Ponca field in Kay County (Oklahoma). The Engler distillation of the original crude as given by Marland Oil Company is as follows[1, 33]: naphtha, 38.9 percent; kerosine, 15.4 percent; gas oil, 16.0 percent; wax distillate, 18.1 percent; bottoms, 10.2 percent. A 600-gallon lot of this oil was first distilled in a semi-commercial column by Sun Oil Company, and the fractions were sent to the National Bureau of Standards. At the laboratory the material was divided into five lots, as received from the refinery, running from the low- to the high-boiling material:

(I) 49.8 percent, represented by about 258 gallons in 73 cuts.
(II) 20.5 percent, represented by about 110 gallons in 31 cuts.
(III) 13.8 percent, represented by about 36 gallons in 22 cuts.
(IV) 10.0 percent, represented by about 20 gallons in 16 cuts.
(V) 5.9 percent, residue; represented by about 10.8 gallons.

1. *Gasoline Fraction*

In the laboratory of the project, the above lot I, including the naphtha fraction and the lower-boiling end of the kerosine fraction, was distilled in a 15-liter metal still provided with a 20-plate column,[1] and subsequently a number of times in 30-plate all-glass rectifying columns.[14] Cuts of nearly constant boiling points were obtained, and further separation by distillation in the then best columns available was no longer practicable, except for that portion normally boiling below 65° C. For the purpose of systematic operation by the several research groups of the project, the following broad classification of fractions was made, according to the normal boiling point of the material: 55-100° C.; 100-130° C.; 130-160° C.; 160-180° C. The higher-boiling fractions were placed in storage.

In separating this material into its constituents, the more or less constant-boiling fractions were subjected to a systematic and interlocking system of fractionation, substantially along the lines indicated by the schematic diagram of Figure 1. From the material boiling in the range 55-180° C., the following hydrocarbons were separated, substantially by a systematic combination of the fractionating processes indicated:

2,3-Dimethylbutane; boiling point, 58.0° C.
2-Methylpentane; boiling point, 60.3° C.
3-Methylpentane; boiling point, 63.3° C.
n-Hexane, boiling point; 68.7° C.

Separated by straight distillation, distillation with methyl and ethyl alcohols, and crystallization with equilibrium melting. Purity* of best samples over 95, 95, 95, and 98 mole percent, respectively.[8, 11]

Methylcyclopentane; boiling point, 71.9° C.

Separated by straight distillation, controlled nitration to remove benzene,† crystallization with equilibrium melting, and distillation with methyl alcohol. Purity of best sample 98.7 mole percent.[13]

2,2-Dimethylpentane; boiling point, 78.9° C.

Separated by straight distillation and crystallization with equilibrium melting. Isolated as a mixture of 54 mole percent of 2,2-dimethylpentane with 46 mole percent of cyclohexane.[20]

Benzene; boiling point, 80.1° C.

Separated by straight distillation, extraction with aniline, and crystallization with equilibrium melting. Total amount of benzene removed from other fractions by controlled nitration.† Purity of best sample 99.8 mole percent.[11]

Cyclohexane; boiling point, 80.8° C.

Separated by straight distillation, controlled nitration to remove benzene,† and crystallization with equilibrium melting. Purity of best sample 99.96 mole percent.[12]

1,1-Dimethylcyclopentane; boiling point, 87.5° C.

Separated by straight distillation and controlled nitration to remove benzene.* Purity of best sample 95 mole percent.[25]

2-Methylhexane; boiling point, 90.0° C.

Separated by straight distillation and crystallization from liquid methane plus propane. Purity of best sample 99.9 mole percent.[25]

3-Methylhexane; boiling point, 91.8° C.

Separation not yet completed.

n-Heptane; boiling point, 98.4° C.
Methylcyclohexane; boiling point, 100.8° C.

Separated by straight distillation, controlled nitration

* With several exceptions, the values of purity given in this section and in Table 2 have been estimated from the freezing curves.[68, 105]
† See discussion on controlled chemical treatment.
* See discussion on controlled chemical treatment.

to remove toluene,* and crystallization with equilibrium melting. Purity of best samples 99.8 and 99.8 mole percent, respectively.[17]

Toluene; boiling point, 110.6° C.

Fractionated by straight distillation. Amount present determined by controlled nitration.* None actually isolated.[9]

2-Methylheptane; boiling point, 117.2° C.

Separated by straight distillation and crystallization from liquid methane plus propane. Purity of best sample 97 mole percent.[26]

Octanaphthene; boiling point, 119.8° C.
1,3-Dimethylcyclohexane; boiling point, 120.3° C.
Octanaphthene (1,2-dimethylcyclohexane?); boiling point, 123.4° C.

Separated by straight distillation and crystallization from liquid methane plus propane. Purity of octanaphthene, boiling point, 119.8° C., not determined; purity of other two, 98 and 91 mole percent, respectively,[39, 47]

n-Octane; boiling point, 125.6° C.

Separated by straight distillation and crystallization with equilibrium melting. Purity of best sample 99.1 mole percent.[10]

Ethylcyclohexane; boiling point, 131.8° C.

Separated by straight distillation, extraction with sulfur dioxide, adsorption with silica gel, distillation with acetic acid, and crystallization from liquid methane plus propane. Purity of best sample 95 mole percent.[41]

2,6-Dimethylheptane; boiling point, 135.2° C.

Separated by straight distillation, extraction with sulfur dioxide, adsorption with silica gel, distillation with acetic acid, and crystallization from liquid dichlorodifluoromethane. Purity of best sample 99 mole percent.[50, 58]

Ethylbenzene; boiling point, 136.2° C.

Separated by straight distillation, extraction with sulfur dioxide, crystallization with equilibrium melting, and controlled sulfonation at 0° C. with subsequent preferential hydrolysis at 30° C. Purity of best sample 95 mole percent.[27]

Nonanaphthene; boiling point, 136.7° C.

Separated by straight distillation, extraction with sulfur dioxide, crystallization from liquid methane plus propane, and crystallization from liquid dichlorodifluoromethane. Purity of best sample better than 99 mole percent.[36]

p-Xylene; boiling point, 138.4° C.
m-Xylene; boiling point, 139.2° C.
o-Xylene; boiling point, 144.4° C.

Separated by straight distillation, extraction with liquid sulfur dioxide, and crystallization with equilibrium melting. The best sample of *m*-xylene was obtained by sulfonation at 0° C. with subsequent preferential hydrolysis at 130° to 135° C. Purity of best samples better than 99.9, 99.9, and 99 mole percent, respectively.[23]

*Iso*nonane; boiling point, 140.8° C.
Nonanaphthene; boiling point, 141.2° C.

Separated by straight distillation, extraction with sulfur dioxide, adsorption with silica gel, distillation with acetic acid, distillation at reduced pressure, crystallization from dichlorodifluoromethane, and crystallization from liquid methane plus propane. Purity of best samples 85 and 95 mole percent, respectively.[36]

4-Methyloctane; boiling point, 142.4° C.
2-Methyloctane; boiling point, 143.3° C.
3-Methyloctane; boiling point, 144.2° C.

Separated by straight distillation, extraction with sulfur dioxide, adsorption with silica gel, distillation with acetic acid, crystallization from dichlorodifluoromethane, and crystallization from liquid methane plus propane. Purity of best samples 80, 99.9, and 95 mole percent, respectively.[55]

n-Nonane; boiling point, 150.7° C.

Separated by straight distillation and crystallization with equilibrium melting. Purity of best sample 99.9 mole percent.[15]

*Iso*propylbenzene; boiling point, 152.4° C.

Separated by straight distillation, adsorption with silica gel, and distillation with acetic acid. Purity of best sample 98.4 mole percent.[61]

1,3,5-Trimethylbenzene (mesitylene); boiling point, 164.6 ° C.
1,2,4-Trimethylbenzene (pseudocumene); boiling point, 169.2° C.
1,2,3-Trimethylbenzene (hemimellitene); boiling point, 176.1° C.

Separated by straight distillation, extraction with sulfur dioxide, extraction with sulfur dioxide plus petroleum ether at —40° C., crystallization from liquid dimethylether, and sulfonation with subsequent preferential hydrolysis to obtain best samples of mesitylene and hemimellitene. Purity of best samples 99.95, 99.9, and 99.95 mole percent, respectively.[32]

n-Decane; boiling point, 174.0° C.

Separated by straight distillation and crystallization with equilibrium melting. Purity of best sample better than 99.99 mole percent.[18]

2. Lubricant Fraction

In 1933 it seemed desirable that, in view of its economic importance to the industry, some information be obtained on the lubricant fraction of petroleum before that material would be reached in the normal course of operation. Accordingly, one unit of the project began work on that part of this Mid-Continent petroleum listed as lot IV, which consisted of about 20 gallons of "lubricant" material representing 10 percent of the original crude petroleum. Of this material there were, as obtained from a distillation in a semi-commercial column by Sun Oil Company, 16 cuts ranging in viscosity at 210° F. from 0.046 to 0.187 stokes (41 to 92 Saybolt seconds).

In the laboratory of the project, this material was then separated into three portions of about equal amounts but of distinctly different properties, substantially by the following procedure: first, an "extract" portion, by batch extraction with liquid sulfur dioxide at about 40° C. (104° F.); second, a "wax" portion, by dewaxing at —18° C. (0° F.) from solution in ethylene chloride; and, third, a "water-white" portion, by treatment of the remaining oil with silica gel.[43]

In this manner there were obtained from the original 67 kg. (20 gallons) of the lubricant fraction, representing 10 percent of this Mid-Continent petroleum, the following three main portions, with the indicated prop-

erties for 100° F. (extrapolated from higher temperatures where necessary):

(a) "Extract" portion, 17.9 kg. in 15 cuts. Viscosity, from 1.9 to 384 stokes (880 to 178,000 Saybolt seconds). Density, from 0.95 to 1.07 g. per cc. Viscosity index, from —150 to —300.

(b) "Wax" portion, 20.3 kg. in 16 cuts. Viscosity, from 0.12 to 0.50 stoke (66 to 231 Saybolt seconds). Density, from 0.80 to 0.83 g. per cc. Viscosity index, from 125 to 150.

(c) "Water-white" portion, 19.8 kg. in 11 cuts. Viscosity, from 0.21 to 1.13 stokes (102 to 520 Saybolt seconds). Density, from 0.85 to 0.88 g. per cc. Viscosity index, 90 to 110.

The third or "water-white" oil portion was the material of greatest immediate interest and importance, and this oil was then subjected to a further separation,[43, 48] There was first carried out a systematic distillation in high vacuum, through eight stages, in order to obtain a series of substantially constant-boiling fractions in which the molecules would be distributed mainly according to their size or molecular weight.

There were obtained in this way 10.1 kg. of "water-white" oil in 22 substantially constant-boiling fractions, the material less viscous than 0.29 stoke (137 Saybolt seconds) and more viscous than 1.15 stokes (530 Saybolt seconds) at 100° F., being placed in storage. The properties of these 22 constant-boiling fractions ranged as follows: viscosity at 100° F., from 0.29 to 1.15 stokes (137 to 530 Saybolt seconds); density at 100° F., from 0.85 to 0.86 g. per cc.; boiling point at 1 mm. mercury from about 200 to 280° C. (392° to 536° F.); viscosity index, from 100 to 92; number of carbon atoms per molecule, from about 27 for the first to 38 for the last fraction. The small change in density and viscosity index, and the large change in viscosity, boiling point, and molecular weight, between the first and last fractions indicated that the systematic distillation had done a fairly good job in separating the material according to size of molecule.

These fractions of substantially constant-boiling oil were then subjected to a separation with respect to type of molecule, by extended reflux extraction with acetone in columns 46 feet long.[48] The lowest-boiling fraction so treated yielded a series of about 30 cuts with an almost constant value of 27.5 for the average number of carbon atoms per molecule, while the value of x in the formula C_nH_{2n+x} ranged from —9 for the most soluble to zero for the least soluble cut; and in this same series the density at 100° F. ranged from 0.90 to 0.82, the viscosity at 100° F. from 0.63 to 0.18 stoke (291 to 89 Saybolt seconds), the boiling point at 1 mm. mercury from 204 to 208° C. (399 to 406° F.) and the viscosity index from 36 to 149. For the highest-boiling fraction so extracted, the following properties were obtained as extremes for the most soluble and the least soluble, respectively, of the series of about 30 cuts obtained from it: average number of carbon atoms per molecule, 38.4 and 36.8; value of x in the formula, C_nH_{2n+x}, —7.4 and —1.95; density at 100° F., 0.883 and 0.846 g. per cc.; viscosity at 100° F., 1.56 and 0.73 stokes (720 and 337 Saybolt seconds); boiling point at 1 mm. mercury, 270 and 275° C. (518 and 527° F.); viscosity index, 75 and 115.

The 10 kg. of "water-white" oil was thus separated into about 600 fractions of from 15 to 20 grams each, at which point the fractionation was stopped because of the lack of material. These fractions, each being about 1/40,000 part of the original crude petroleum, were extremely narrow cuts with respect to both types and size of molecules.[49]

VI. SUMMARY OF THE RESULTS OBTAINED ON THE NAPHTHA FRACTION

1. *Hydrocarbons in the Naphtha Fraction*

In Table 2 are listed, for that part of this Mid-Continent petroleum normally boiling below 180°C. (356°F.), the hydrocarbon constituents as determined by A.P.I. Research Project 6 to September 1, 1937. The columns in the table give, respectively, the number, molecular formula, name, boiling point at 1 atmosphere, purity of the best sample, estimated relative amount by volume in the crude, and reference to the research paper in which the given hydrocarbon is reported.

2. *Estimated Amounts of the Hydrocarbons*

In connection with the values which have been given for the estimated amount of a given hydrocarbon in the crude petroleum, it is important to note the following points:

(a) Compared with the actual isolation of the pure hydrocarbons, the estimation of the amount of a given hydrocarbon in the crude petroleum is of secondary importance, and is based upon the amounts of the hydrocarbon obtained in various degrees of estimated purity. Owing to the fact that a given lot of material may be subjected to many different processes of fractionation before the separation is successfully effected, considerable losses of material occur at various stages in the work. These operational losses take place over a period of years, and it is impossible to evaluate them accurately. Any values deduced for the estimated amount of a given hydrocarbon in the crude petroleum must, therefore, be considered to be roughly approximate and to give only the order of magnitude. The values for the estimated amount of a given hydrocarbon in the crude petroleum which have so far been published by the project have been based upon the original volume of the crude petroleum. However, even when allowance is made for immediate operational losses occurring in the separation of a given hydrocarbon, the foregoing procedure takes no cognizance of the general losses which have occurred over broad fractions of material during the years of processing.

(b) A more accurate quantitative measure of the amounts of the various hydrocarbons in this Mid-Continent petroleum can be obtained by carrying out, on a second lot of the original material, an "incomplete" separation, in which an accurate material balance is kept, and utilizing the results of the more complete and exhaustive separation already reported to interpret the data so obtained. The procedure would be as follows: first, the material would be distilled systematically in highly-efficient rectifying columns (keeping an accurate record of quantities of oil) in order to obtain a series of substantially constant-boiling fractions; second, appropriate tests would be made on these constant-boiling fractions, based upon the information already available from the exhaustive fractionation, in order to ascertain the composition of the given fractions; third, the data obtained in this "short-cut" method would be correlated with the data from the complete separation to yield more reliable values for the amounts of the hydrocarbons in this petroleum. A procedure such as this has already been applied to the naphtha fraction of Mid-Continent petroleum from the Ponca City field by Fenske and collaborators,[96, 101] and it is hoped that the results of this study will lead to more accurate values for the amounts of the various hydrocarbons in the crude.

(c) Pending further study of the problem of a more accurate evaluation of the actual amount of a given hydrocarbon in this crude petroleum, there are reported in Table 2, in the list of hydrocarbons in a Mid-Conti-

TABLE 2

Hydrocarbons in a Mid-Continent Petroleum as Determined by American Petroleum Institute Research Project 6 at the National Bureau of Standards

(To September 1, 1937)

No	Formula	Name and Type of Hydrocarbon	Boiling Point at 1 Atmosphere (Deg. C.)	Purity of Best Sample Isolated (Mole Percent)	Estimated Relative Amount by Volume [a]	For Description, See the Following References [b]
		PARAFFINIC				
1	CH_4	Methane	−161.7	[c]	[c]	..
2	C_2H_6	Ethane	− 88.6	[c]	[c]	..
3	C_3H_8	Propane	− 42.2	[c]	[c]	..
4	C_4H_{10}	*Iso*butane	− 12.1	[c]	[c]	..
5	C_4H_{10}	*n*-Butane	− 0.5	[c]	[c]	..
6	C_5H_{12}	2-Methylbutane	27.9	[c]	[c]	..
7	C_5H_{12}	*n*-Pentane	36.1	[c]	[c]	..
8	C_6H_{14}	2,3-Dimethylbutane	58.0	>95.	0.06	8,11
9	C_6H_{14}	2-Methylpentane	60.3	>95.	0.1_2	8,11
10	C_6H_{14}	3-Methylpentane	63.3	>95.	0.2_5	8,11
11	C_6H_{14}	*n*-Hexane	68.7	98.3	0.7	8,11
12	C_7H_{16}	2,2-Dimethylpentane	78.9	54.	0.04	20
13	C_7H_{16}	2-Methylhexane	90.0	99.9	0.3_5	25
14	C_7H_{16}	3-Methylhexane	91.8	[d]	0.2	[d]
15	C_7H_{16}	*n*-Heptane	98.4	>99.8	1.1	17
16	C_8H_{18}	2-Methylheptane	117.2	97.	0.5	26,47
17	C_8H_{18}	*n*-Octane	125.6	99.1	1.0	10
18	C_9H_{20}	2,6-Dimethylheptane	135.2	>99.	0.1	50,58
19	C_9H_{20}	*Iso*nonane	140.8	85.	0.05	63
20	C_9H_{20}	4-Methyloctane	142.4	80.	0.06	55
21	C_9H_{20}	2-Methyloctane	143.3	99.9	0.2	55
22	C_9H_{20}	3-Methyloctane	144.2	95.	0.06	55
23	C_9H_{20}	*n*-Nonane	150.7	99.9	1.0	15
24	$C_{10}H_{22}$	*n*-Decane	174.0	>99.99	0.8	18
		NAPHTHENIC				
25	C_5H_{10}	Cyclopentane	49.5	[c]	[c]	..
26	C_6H_{12}	Methylcyclopentane	71.9	98.7	0.2_5	13
27	C_6H_{12}	Cyclohexane	80.8	99.96	0.3_5	12
28	C_7H_{14}	1,1-Dimethylcyclopentane	87.5	95.	0.05	25
29	C_7H_{14}	Methylcyclohexane	100.8	>99.8	0.3_5	17
30	C_8H_{16}	Octanapthene	119.8	[c]	0.2	47
31	C_8H_{16}	1,3-Dimethylcyclohexane	120.3	98.		39,47
32	C_8H_{16}	Octanaphthene (1,2-dimethylcyclohexane?)	123.4	91.	0.04	47
33	C_8H_{16}	Ethylcyclohexane	131.8	95.	0.1	41
34	C_9H_{18}	Nonanapthene (alkyl cyclopentane)	136.7	>99.	0.1	36
35	C_9H_{18}	Nonanapthene	141.2	95.	0.08	63
		AROMATIC				
36	C_6H_6	Benzene	80.1	99.8	0.08	11
37	C_7H_8	Toluene	110.6	[c]	0.3	9
38	C_8H_{10}	Ethylbenzene	136.2	95.	0.03	27
39	C_8H_{10}	*p*-Xylene	138.4	>99.9	0.04	23
40	C_8H_{10}	*m*-Xylene	139.2	>99.9	0.1_2	23
41	C_8H_{10}	*o*-Xylene	144.4	>99.	0.1_2	23
42	C_9H_{12}	*Iso*propylbenzene	152.4	98.4	0.03	61
43	C_9H_{12}	1,3,5-Trimethylbenzene (mesitylene)	164.6	99.95	0.02	32
44	C_9H_{12}	1,2,4-Trimethylbenzene (pseudocumene)	169.2	99.9	0.2	32
45	C_9H_{12}	1,2,3-Trimethylbenzene (hemimellitene)	176.1	99.95	0.06	32

[a]—The numbers in this column give the estimated relative amounts by volume of the given hydrocarbon in the petroleum, referred to normal octane or normal nonane (which are present in substantially equal amounts) as unity. In order to obtain the order of magnitude of the *percentage content* of the given hydrocarbon in the original crude, these figures should be multiplied by a factor which is roughly estimated to be somewhere between 1 and 1 2-3 (see text on p. 15).

[b]—See list of publications of API Research Project 6.

[c]—Not determined.

[d]—Determination not yet completed.

nent petroleum determined by A.P.I. Research Project 6, not values of the percentage amount of a given hydrocarbon in the crude petroleum, but values of the *estimated relative amounts, by volume, of the given hydrocarbons in the petroleum.* While any one of these values may be in error by as much as 50 to 100 percent of itself, the uncertainties probably average out over the entire lot so as to give a fairly good quantitative picture of the relative amounts of the hydrocarbons in the crude or in the gasoline fraction. The values for normal octane and normal nonane, which appear rather definitely to be present in about equal amounts in this crude,[10, 15, 101] are each assigned a value of 1.0, and the others corresponding relative numbers. The order of magnitude of the amount of the given hydrocarbon in the original crude petroleum can be obtained by multiplying the numbers giving the relative amounts (in terms of normal octane or normal nonane) by a factor which may be roughly estimated, at this time, to be somewhere between 1 and 1 2/3.

3. *Number of Significant Constituents in Petroleum*

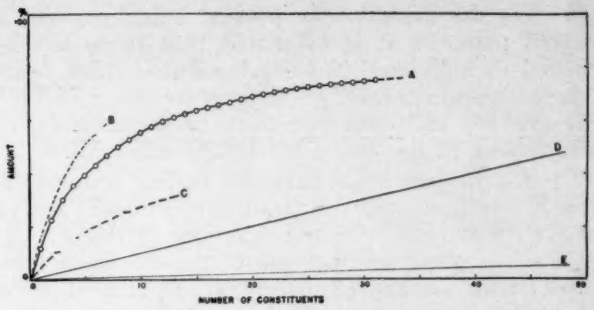
Ever since the beginning of research on the chemical constitution of petroleum many decades ago, one of the most interesting but perplexing questions has been: "How many hydrocarbons are there in petroleum?" It is likely that this question can never be answered literally; but, from the work which has so far been done, a partial answer may now be given with respect to a large part of the gasoline fraction of Mid-Continent petroleum.

In Table 2 there are listed 45 hydrocarbons definitely known to be in that part of this petroleum normally boiling below 180°C. The question immediately arises as to how many more significant constituents there may be in this material. Since a large part of the material normally boiling between 145 and 180°C. remains to be resolved, the best results in the present analysis of the number of significant constituents is obtained by considering only the material normally boiling between 55 and 145°C. which material, on the basis of the present volume of unresolved fractions, appears to be over three-fourths assigned to individual hydrocarbons. Accordingly, there are listed in Table 3 the 31 hydrocarbons, taken in decreasing order of abundance, which have been separated from the fraction 55-145°C. (131-

293°F.). The last two columns in Table 3 give, respectively, the relative amount of each hydrocarbon and the summation of the relative amounts.

As noted above, the amount of the fraction 55-145°C. which, on the basis of the present volume of the unresolved material, has been assigned to individual hydrocarbons is over 75 percent. Assuming, then, that the summation value of 7.0 is 75 percent of the total fraction, 100 percent would be 9.3; and it follows, within the accuracy of these data and assumptions, that 8 individual hydrocarbons constitute about one-half of the entire petroleum normally boiling between 55 and 145°C. (131-293°F.). And, similarly, 18 hydrocarbons constitute about two-thirds of the fraction 55-145°C. These numbers 8 and 18 are to be compared with the number 100, which represents approximately the total number of known paraffin, naphthene, and aromatic hydrocarbons normally boiling between 55 and 145°C.; and with the number 1000, which gives the order of magnitude of the total number of *possible* hydrocarbons of these three classes that would be expected to boil between 55 and 145°C. at atmospheric pressure.

The values shown in Table 3 are plotted in Figure 3 as Curve **A**. On the scale of ordinates is plotted the summation of the relative amounts of *n* hydrocarbons in the fraction 55-145°C., and on the scale of abscissae is plotted *n*, the number of hydrocarbons in the fraction 55-145°C. taken in decreasing order of abundance. Following the discussion given above, the 100-percent line on this chart is located at such a place that the total summation of the 31 hydrocarbons is 75 percent. The curve **A** then represents the relation between number of hydrocarbons taken in decreasing order of abundance and the amount of the fraction 55-145°C. which is estimated to be constituted by the given number of hydrocarbons, all within the limits of accuracy of the above data and assumptions. For example, curve **A** indicates that, of the fraction 55-145°C., three fourths of the oil is constituted by approximately 31 hydrocarbons, two thirds by about 18 hydrocarbons, one half by about 8, one third by 4, and one fifth by 2. That is to say, while there may actually be thousands of hydrocarbons in this fraction (indicated by the curve going to large values along the horizontal axis, for 100 percent of the material) the major part of the material is constituted by a rather small number of constituents.



The scale of ordinates gives the estimated amount of the fraction 55-145° C. which is constituted by a given number of constituents; and the scale of abscissae gives the number of constituents taken in order of abundance.

Curve "A" represents the estimated amounts of the fractions 55-145° C. which is constituted by the various numbers of hydrocarbons, from 1 to 31, actually separated from this fraction of Mid-Continent petroleum, which hydrocarbons are taken in order of abundance. The estimates of amount are based on the values given in Table 3 and on certain assumptions discussed in the text.

Curve "B" indicates the relation which would obtain for the 55-145° C. fraction of a petroleum containing very large amounts of the normal paraffin hydrocarbons (see text above).

Curve "C" indicates the relation which would obtain for the 55-145° C. fraction of a "complex" petroleum containing no one hydrocarbon in large amount.

Curves "D" and "E" indicate the relations which would obtain for mixtures of equal amounts of 100 and 1,000 hydrocarbons, respectively (see text below).

FIGURE 3

Plot Showing the Relation Between the Number of Constituents, and Their Estimated Amounts, in that Fraction of Petroleum Normally Boiling Between 55 and 145° C. (131 and 298° F.).

Curve **B**, in Figure 3, illustrates the nature of such a relation for a similar fraction from petroleum from the Mt. Pleasant field, in Michigan, which contains very large amounts of the normal paraffin hydrocarbon.[96, 101] Curve **C**, in Figure 3, would be indicative of a very complex crude containing no one hydrocarbon in large amount. The line **D** indicates the kind of petroleum fraction which nature might have prepared had there been produced together in equal amounts all the approximately 100 paraffin, naphthene, and aromatic hydrocarbons, normally boiling in the range 55-145°C., which are at present known to man. Similarly, line **E** represents the petroleum fraction which nature would have prepared had she produced together in equal amounts all of the approximately 1000 possible (order of magnitude only) paraffin, naphthene, and aromatic hydrocarbons which would be expected to boil normally in the range 55-145°C.

4. *Conclusions Concerning the Constitution of the Naphtha Fraction*

In connection with the work which has so far been done on that part of this Mid-Continent petroleum normally boiling below 180°C. (356°F.) the following summary may be made*:

TABLE 3

Hydrocarbons Separated from the Fraction of Petroleum Normally Boiling Between 55 and 145° C. Taken in Decreasing Order of Abundance

No.	Formula	Hydrocarbon	Boiling Point at 1 Atmosphere (Deg. C.)	Estimated Relative Amount by Volume [a]	Summation of the Estimated Relative Amounts by Volume
1	C_7H_{16}	*n*-Heptane	98.4	1.1	1.1
2	C_8H_{18}	*n*-Octane	125.6	1.0	2.1
3	C_6H_{14}	*n*-Hexane	68.7	0.7	2.8
4	C_8H_{18}	2-Methylheptane	117.2	0.5	3.3
5	C_7H_{16}	2-Methylhexane	90.0	0.3!	3.6_5
6	C_6H_{12}	Cyclohexane	80.8	0.3!	4.0
7	C_7H_{14}	Methylcyclohexane	100.8	0.3!	4.3_5
8	C_7H_8	Toluene	110.6	0.3	4.6_5
9	C_6H_{14}	3-Methylpentane	63.3	0.2!	4.9
10	C_6H_{12}	Methylcyclopentane	71.9	0.2!	5.1_5
11	C_7H_{14}	3-Methylhexane	91.8	0.2	5.3_5
12	C_9H_{20}	2-Methyloctane	143.3	0.2	5.5_5
13	C_6H_{14}	2-Methylpentane	60.3	0.1!	5.6_7
14	C_8H_{10}	*m*-Xylene	139.2	0.1!	5.7_9
15	C_8H_{10}	*o*-Xylene	144.4	0.1!	5.9_1
16	C_9H_{20}	2,6-Dimethylheptane	135.2	0.1	6.0_1
17	C_8H_{16}	Octanaphthene	119.8	(0.1)	6.1_1
18	C_8H_{16}	1,3-Dimethylcyclohexane	120.3	(0.1)	6.2_1
19	C_8H_{16}	Ethylcyclohexane	131.8	0.1	6.3_1
20	C_9H_{18}	Nonanaphthene (alkyl cyclopentane)	136.7	0.1	6.4_1
21	C_6H_6	Benzene	80.1	0.08	6.4_9
22	C_9H_{18}	Nonanapththene	141.2	0.08	6.5_7
23	C_6H_{14}	2,3-Dimethylbutane	58.0	0.06	6.6_3
24	C_9H_{20}	4-Methyloctane	142.4	0.06	6.6_9
25	C_9H_{20}	3-Methyloctane	144.2	0.06	6.7_5
26	C_9H_{20}	*Iso*nonane	140.8	0.05	6.8
27	C_7H_{14}	1,1-Dimethylcyclopentane	87.5	0.05	6.8_5
28	C_7H_{16}	2,2-Dimethylpentane	78.9	0.04	6.8_9
29	C_8H_{16}	Octanaphthene (1,2-dimethylcyclohexane?)	123.4	0.04	6.9_3
30	C_8H_{10}	*p*-Xylene	138.4	0.04	6.9_7
31	C_8H_{10}	Ethylbenzene	136.2	0.03	7.0

[a]—See text for explanation. Amounts are based on normal octane as unity.

* All estimates of quantity are based on the assumptions discussed on p. 15.

(a) On the basis of the present volume of the unresolved material, it is estimated that there has been assigned to individual hydrocarbons over three fourths of the petroleum normally boiling in the range 55-145°C. (131-293°F.) and over one third of the material normally boiling in the range 145-180°C. (293-356°F.).

(b) All the petroleum normally boiling below 180°C. (356°F.) is composed of paraffin, naphthene, and aromatic hydrocarbons. In the fraction 55-180°C. (131-356°F.), the respective amounts of these three classes of hydrocarbons are approximately 60, 30, and 10 percent.

(c) The difficulty of separating the various hydrocarbons is least for the normal paraffins, somewhat greater for the aromatics, and greatest for the branched-chain paraffins and the naphthenes.

(d) From the material normally boiling below 180°C., there have been separated 45 different hydrocarbons (24 paraffins, 11 naphthenes or cycloparaffins, and 10 aromatics).

(e) It is estimated that approximately one half of the entire material normally boiling between 55 and 180°C. (131-356°F.) is constituted by about 12 hydrocarbons.

(f) Of the paraffin hydrocarbons, there have so far been obtained 4 of the 5 possible isomers of hexane, 4 of the 9 heptanes, 2 of the 18 octanes, 6 of the 35 nonanes, and 1 of the 75 decanes.

(g) All of the possible aromatic hydrocarbons boiling below 153°C. viz., benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene, *o*-xylene, and *iso*propylbenzene, have been found. Each of the three trimethylbenzenes, mesitylene (164.6°C.) pseudocumene (169.2°C.), and hemimellitene (176.1°C.) have also been isolated. In addition, preliminary work indicates the presence of *n*-propylbenzene and each of the three methylethylbenzenes, which normally boil between about 154 and 164°C.

(h) It is estimated that the normal paraffin hydrocarbons from hexane to decane, inclusive, together constitute about one third of all this petroleum normally boiling between 55 and 180°C. (131-356°F.).

(i) After the normal paraffins, the next more abundant hydrocarbons of the fraction 55-180°C. (131-356°F.) include: 2-methylheptane, cyclohexane, methylcyclohexane, toluene, 2-methylhexane, pseudocumene, methylcyclopentane, 3-methylhexane, 3-methylpentane, and 2-methyloctane, the least abundant of which is estimated to constitute over 1 percent of the fraction 55-180°C. (131-356°F.).

(j) With the exception of those molecules having five or fewer carbon atoms per molecule, and seven others indicated in Table 2, all the hydrocarbons listed in Table 2 were obtained with a purity of 95 mole percent or better. Three of the others were obtained with purities of 80, 85, and 91 mole percent, respectively.

(k) Of the hydrocarbons listed in Table 2, 25 have not previously been actually isolated from any petroleum—the evidence for their presence, where reported, having been in most instances based upon the products obtained by chemical treatment of certain petroleum fractions or upon volume peaks in the distillation curve.

VII. SUMMARY OF THE RESULTS OBTAINED ON THE LUBRICANT FRACTION

In reviewing the results of the work of the project on the lubricant fraction of petroleum, it is well to note that, as regards individual compounds, the chemical constitution of various fractions of petroleum appears to increase in complexity almost geometrically with increase in molecular weight or size of molecules in the given fractions. For example, the hydrocarbons in the lubricating-oil fraction of petroleum contain, on the average, about four or five times as many atoms per molecule as those in the gasoline fraction; and the number of possible isomers of triacontane, $C_{30}H_{62}$, is over 4,000,000,000; while for octane, C_8H_{18}, the number is only 18.

As indicated above, the lubricant fraction of this Mid-Continent petroleum was separated into three broad fractions of nearly equal portions: "extract," "wax," and "water-white" oil. The "water-white" oil was subjected first to a systematic distillation and then to a systematic extraction, resulting in about 600 fractions (15 to 20 grams each) "homogeneous" with respect to type and size of molecules. Each of these fractions constitutes about 1/4000 part of the original lubricant fraction and about 1/40,000 part of the original crude petroleum and, while not pure compounds, are probably nearer to pure hydrocarbons than any material hitherto obtained from any lubricating oil.

In view of the fact that these fractions are "homogeneous" mixtures containing molecules of the same type and size, the procedure discussed on p. 10 concerning the identification of extremely narrow cuts according to type of molecule was followed. Measurements were made of eight important physicochemical properties, and these were correlated with those of pure hydrocarbons of known structure.[49]

As a result of these correlations, the following conclusions have been made concerning the chemical constitution of the 600 fractions of "water-white" oil obtained from the original lubricant fraction by successively extracting the material soluble in sulfur dioxide at about 40°C. (104°F.), removing the "wax" by crystallization from ethylene chloride at —18°C. (0°F.), obtaining a "water-white" oil by filtration through silica gel, distilling systematically in high vacuum, and separating by reflux extraction with acetone:[49]

1. Of the fractions of lowest molecular weight, with about 28 carbon atoms per molecule, the least soluble (in acetone) fractions consist substantially of one-ring naphthene (cycloparaffin) hydrocarbons, and the more soluble fractions consist of naphthenes with two, and some with three, rings per molecule, each with the appropriate number of paraffin side chains.

2. Of the fractions of highest molecular weight, with about 37 carbon atoms per molecule, the least soluble consist substantially of two-ring naphthenes (cycloparaffins); and the more soluble fractions consist of naphthenes with three, and some with four, rings per molecule, each with the appropriate number of paraffin side chains.

3. Because of some incompleteness in the separation, the most soluble fractions appear to contain some unsaturated hydrocarbons and an appreciable amount of one-ring aromatic hydrocarbons.

4. No evidence exists to indicate the presence of *iso*- or branched-chain paraffins in this "water-white" oil.

5. It is expected that most of the aromatic hydrocarbons will separate in the sulfur-dioxide "extract" along with the multi-ring naphthenes.

VIII. WORK IN PROGRESS

On its current schedule, the project has the following problems:

1. *The investigation of the chemical constitution of the "extract" portion of the lubricant fraction of this Mid-Continent petroleum.* This work is being done in a manner similar to that employed on the "water-white" oil portion of this same lubricant fraction, and involves

the exhaustive resolution of the material into fractions "homogeneous" with respect to type and size of molecule, the measurement of the important physical properties, and the correlation of these properties with those of pure hydrocarbons of known structure in order to deduce the nature of the hydrocarbons in this material. The work so far accomplished[73] on this problem includes the separation of the original "extract" into two portions by dissolving the "extract" in liquid sulfur dioxide and successively extracting, by batch operation, the material soluble in petroleum ether at —50°C. (—58°F.). This material soluble in petroleum ether at —50°C. has been subjected to a systematic distillation in high vacuum through eight stages and, subsequently, separated by reflux extraction with methyl cyanide (plus some acetone for the less soluble fractions) in columns 55 feet long. This material had, before the distillation in high vacuum, a nitrogen content of about 0.13 percent and a sulfur content of about 0.9 percent; and the data obtained will show how the distribution of the nitrogen and of the sulfur, respectively, among the various fractions will be affected, first by the systematic distillation in high vacuum and, second, by the systematic extraction.[73] In this work there have been obtained about 175 final fractions (of from 15 to 20 grams), each of which represents about 1/4,000 part of the original lubricant fraction and about 1/40.000 part of the original crude petroleum. Of these 175 fractions, 30 have been designated "key" fractions; and on these, where possible, are being determined the following properties:[73] molecular weight, carbon and hydrogen content, nitrogen content, sulfur content, viscosity at 100 and 210°F., density, refractive index, refractive dispersion, optical activity, boiling point at 1 mm. mercury pressure, and aniline point. When all these data have been obtained, the correlation with the properties of pure hydrocarbons of known structure will be made in order to determine the exact nature of these compounds, which are expected to be highly aromatic and multi-ring naphthene hydrocarbons.

2. *The isolation and identification of pure aromatic hydrocarbons (suspected to be* n-*propylbenzene, 1,2-methylethylbenzene, 1,3-methylethylbenzene, and 1,4-methylethylbenzene) from the mixture of aromatic hydrocarbons occurring in that part of the gasoline fraction normally boiling between about 152 and 162°C.* This aromatic concentrate has a volume of about 4 liters, and was separated from the approximately 20 liters of the normal mixture of paraffin, naphthene, and aromatic hydrocarbons occurring in this boiling range, by distillation with acetic acid and treatment with silica gel.[62] The fractionation processes expected to be used to resolve this mixture into its constituents include distillation, crystallization and, if necessary, carefully-controlled sulfonation followed by preferential hydrolysis to recover the hydrocarbons, a procedure which was successfully used to separate ethylbenzene and the xylenes.[23, 27]

3. *The exhaustive fractionation of a large quantity (240 gallons of the dewaxed lubricant fraction of a Mid-Continent crude, with the aim of separating pure hydrocarbons of high molecular weight.* This work was begun by one unit of the project nearly a year ago.[100] Through the courtesy of Continental Oil Company, there was obtained 6 barrels of untreated, distilled, dewaxed (with benzol plus ethylene chloride as solvent) lubricant fraction of a Mid-Continent petroleum from the Oklahoma City field, 3 barrels of "raw 450 distillate," and 3 barrels of "raw 150 distillate," having viscosities at 100°F. of about 450 and 150 Saybolt seconds, respectively. These two cuts of oil were mixed together, one to one (approximately the production ratio) in order to obtain a mixture having a composition, with the exception of the removed wax, substantially the same as that of the corresponding fraction in the natural crude. Sun Oil Company kindly ran 240 gallons of this oil in a semi-plant column at Marcus Hook, Pennsylvania. Ten passes of the oil were made through their still under vacuum (5 to 8 mm. mercury), and 11 fractions were obtained—nine 10 percent distillation cuts, a residue, and "hold-up." About 80 gallons of this oil has been left unfractionated, subject to future reference. Of the nine distillation fractions of this oil as obtained from the semi-commercial still, the properties of the lightest and heaviest fractions, respectively, were as follows: viscosity at 100°F., 0.173 and 1.58 stokes (86 to 730 Saybolt seconds); density at 100°F., 0.875 and 0.893 g. per cc.; refractive index, n_D^{25}, 1.492 and 1.502; boiling point at 1 mm. mercury, 159 and 238°C. (318 and 460°F.); viscosity index, 78 and 60. In the laboratory of the project at the National Bureau of Standards, there was built a high-vacuum, metal distillation column, 6 inches in diameter and about 7 feet long, for carrying out a rectification of this oil in high vacuum (pressure less than 0.001 mm. mercury at the outlet of the condenser). The 240 gallons of oil has received one systematic distillation through this column, and the second stage is well under way. When the oil has been separated into substantially constant-boiling fractions, it is planned next to subject the material to a systematic process of extraction.[100]

IX. FUTURE WORK

In connection with the future work of the project, some important fractions of petroleum await investigation, and included in this work are the following problems:

1. *The separation of the mixture of branched-chain paraffins and naphthene hydrocarbons occurring in the normal boiling range 145-160°C.* From that part of the original material normally boiling in this range, there have already been separated the pure hydrocarbons, normal nonane [15] and *iso*propylbenzene,[61] and the aromatic concentrate now under investigation, leaving as material remaining for future work the mixture of branched-chain paraffins and naphthene hydrocarbons. This is about the lowest-boiling range in which there is a possibility of finding naphthenes with a "strutted" structure.

2. *The separation of the material (a mixture of naphthenes and branched-chain paraffins, and some aromatic concentrate) remaining in the range 160-180°C.* From that part of the original petroleum normally boiling in this range, there have been separated the pure hydrocarbons, normal decane[18] and each of the three trimethylbenzenes,[32] leaving the above mixture of *iso*paraffins and naphthenes, and some aromatic concentrate, for future investigation. Some of the hydrocarbons normally boiling near this range, and which may possibly be found in the oil, include the butyl-, methylpropyl-, diethyl-, and dimethylethylbenzenes, mono- and bicyclic-naphthenes of 10 carbon atoms, and branched-chain decanes.

3. *The further resolution of certain relatively small "recalcitrant" fractions, containing* iso*paraffins and naphthenes, still remaining in the range below 145°C.* While all the petroleum normally boiling below 145°C. is considered substantially worked out, there remain certain concentrates containing *iso*paraffins or naph-

thenes, or both, which may respond to the more newly-developed methods of separation, and should be subject to future work. These include fractions at 91-92°C., 110-112°C., 126-128°C., and 132-138°C.

4. *The investigation of the hydrocarbons in the kerosine fraction of petroleum.* So far in the work of the project, no material containing hydrocarbons with from 11 to about 25 carbon atoms per molecule has been subjected to investigation, and the kerosine fraction appears to be promising material for the opening wedge into this little-explored region of petroleum hydrocarbons. In this material, as contrasted with the gasoline fractions, there is the possibility not only of many more isomers but also of combination structures involving paraffin, naphthene, and aromatic groups.

One of the most important phases of the future work of the project in its primary business of separating petroleum into its constituents (as indicated by the specific problems listed above) will be the improvement, to a higher degree of efficiency, of the existing laboratory methods of fractionation, and the development of new ones, in order to cope effectively with the more difficultly-separable fractions which are in the offing.

At the present time the processes of fractionation commonly used in industry and various research and development laboratories are those of distillation, crystallization, extraction, adsorption, and certain variations and combinations of them. These processes are based upon the following properties as "vulnerable" to the given fractionation: boiling point, freezing point, solubility in various solvents, susceptibility to adsorption on appropriate solids, and ability to form azeotropic mixtures. In addition to the foregoing processes of fractionation there are two others less widely used: molecular distillation,[1, 43, 106] at very low pressures, in which the fractionation depends primarily upon the respective ratios of the vapor pressure to the square root of the molecular weight of the constituents; and centrifuging at extremely high speeds,[108, 109] in which the fractionation depends primarily upon the density of the various constituents. The latter two methods have so far been used mainly in the fractionation of biologically-important substances, but there is no reason why these processes cannot be extended to mineral oils, provided sufficiently worthwhile constituents can be separated by their use. In developing a new process of fractionation which may be even more effective for certain problems than the existing processes, there must first be selected an appropriate physical property which has significantly-different values for the various constituents to be separated, and then there must be devised a workable apparatus to whose operation the given property is a "vulnerable" one.

Another important phase of the future work of the project lies in the field relating to the determination of the physicochemical properties of pure hydrocarbons, for record and identification; and of mixtures of hydrocarbons, for characterization and for indicating the extent of fractionation resulting from a given process of separation. Efforts in this direction will involve the adaptation to these uses of old methods of measurement and of newly-developed methods which appear applicable to this work.

X. CONCLUSION

Although investigations on the nature of petroleum have been going on for many decades, it was not until about 20 years ago that the petroleum industry itself began to consider seriously the chemical constitution of its raw material. With a few notable exceptions, the researches on the chemical constitution of petroleum had been sporadic and casual; and, relative to the importance, magnitude, and complexity of the problem, greatly limited in scope. A dozen years ago there were a number of hydrocarbons whose presence in the gasoline fraction of petroleum was reported, but for molecules of more than five carbon atoms the evidence was in most cases based upon the products obtained by chemical treatment of certain petroleum fractions or upon volume peaks in the distillation curve. What was needed was a comprehensive and unified investigation of the chemical constituents based upon the actual isolation of pure hydrocarbons from the crude oil. In reviewing the cooperative research on the chemical constitution of petroleum which has been carried on since 1927 by the American Petroleum Institute and the National Bureau of Standards, it appears that considerable farsightedness was manifested by the sponsors in initiating such a project at that time. No other single move could have been better calculated to impart such a healthy impulse to the growth of various other researches in or important to the petroleum industry.

For some years there has been under way in the industry a transition from the production of a few exceedingly broad fractions of petroleum, having general properties, to the manufacture of many different narrow cuts having specialized properties. The general properties of each of the broad fractions have been such as to satisfy fairly well the requirements of a number of different services; but the need for greater efficiency, higher speeds, and more concentrated power, the use of high pressures and high and low temperatures, and the invention and development of devices for improving the comfort and welfare of man, inevitably leads to the necessity of manufacturing materials of specialized properties which can better fill the ever-expanding and more exacting requirements of today.

The wresting from nature of knowledge of the chemical constitution of petroleum, with the attendant development and improvement of methods of fractionation and measurement of properties, serves the petroleum industry in two ways. First, there are provided data and information which can be utilized by the industry to improve the control and economy of the processes used for producing the broad fractions (gases, gasoline, fuel oil, and lubricants) which are the bulwark of the industry at the present time. Second, there is provided a knowledge of the available hydrocarbons in petroleum, and of methods for effecting their separation, which is a necessary requirement in the manufacture of fractions having specialized properties, and in the development of a petroleum chemical industry, which must deal with substantially pure hydrocarbons or with highly-fractionated "homogeneous" material.

The petroleum chemical industry, whose "coming of age" may be said to have been celebrated by the symposium on the "Chemical Utilization of Petroleum Hydrocarbons" held by the Division of Petroleum Chemistry of the American Chemical Society, at Rochester, New York, in September of this year, is a development following naturally from the combined effects of a number of causes. The first of these may be taken as the work of determining the identity and approximate amount of the significant hydrocarbons actually in petroleum; the second is the development of processes of fractionation which can be used economically on a commercial scale to effect the separation of wanted hydrocarbons; and the third is the accumulation of information on the chemical thermodynamic and kinetic constants of hydrocarbons and their derivatives. As far as the development of the petroleum chemical industry is

concerned, any one of the factors just mentioned would be of no avail in the absence of the other two.

At the current prices listed by chemical supply houses for the best hydrocarbons (boiling ranges 0.5 to 2°C.) regularly-purchasable for laboratory use, 20 gallons of a Mid-Continent "straight-run" gasoline, having a wholesale value of about $1.00, has a potential value of about $1,000 in terms of the amounts of the five normal paraffin hydrocarbons, *n*-hexane to *n*-decane, inclusive, which can be separated from it. When the existing laboratory methods for separating hydrocarbons from petroleum are successfully worked out on a commercial scale, the cost of producing these hydrocarbons will be considerably less than those of other processes, synthetic or otherwise. The petroleum chemical industry is now successfully utilizing methane, ethane, propane,*n*-butane, *iso*butante, *n*-pentane,, *iso*-pentane, ethylene, propylene, *n*-butene, and *iso*butene, to produce alcohols, glycols, ethers, oxides, aldehydes, ketones, esters, acids, anhydrides, chlorinated compounds, amines, resins, "*iso*octane" motor fuel, etc., by the various processes of polymerization, depolymerization, hydrogenation, dehydrogenation, oxidation, halogenation, hydration, dehydration, and "alkylation."[103] It is apparent that the range of products can be enormously increased once the use of hydrocarbons of higher molecular weight (six and more carbon atoms) as starting material is made commercially possible by their separation from petroleum. Judging from the recent reports of several groups of investigators,[101, 104] it appears that the separation of a number of important hydrocarbons of more than five carbon atoms per molecule from the gasoline fraction, on a semi-commercial scale and in a state of relatively high purity, is now an accomplished fact.

The researches necessary to carry on a petroleum chemical industry, whose purpose is substantially that of achieving a more economic utilization of petroleum, may logically be divided into two groups: 1, fundamental researches and, 2, applied researches. The fundamental researches include: *a*, the investigation of the chemical constitution of petroleum and, *b*, the determination of the chemical thermodynamic and kinetic constants of hydrocarbons and their derivatives; and the applied researches include: *a*, the development of practical commercial methods for effecting the separation of wanted hydrocarbons and, *b*, the investigation of various chemical reactions involving petroleum hydrocarbons and their derivatives for the purpose of obtaining new and desirable substances for the manifold needs of man. The fundamental researches ought properly to be carried on and encouraged in the university and government laboratories, leaving the competitive research and development units of the industry to make practical application of the knowledge and data obtained by the non-profit laboratories. The system should be a self-perpetuating one wherein the industry, profiting from its applications of the basic knowledge and data, would be anxious to assure the continued flow into the proper channels of resources for researches on base-line problems.

XI. BIBLOGRAPHY

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Materials Control *In the* Laboratory

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THE modern refinery control laboratory makes use of a diversified line of materials and supplies. The quantity of any one item is not likely to be large compared with the demands of colleges and other institutions but the number of items makes stock maintenance a problem.

Such diversity is necessary because the laboratory is called upon to perform a wide variety of tests. There may be any number of methods locally developed by experience as aids in plant processing. For marketing purposes the industry accepts the ASTM procedures which comprise over 50 standard methods for testing petroleum products and lubricants. In addition, many large consumers such as steel companies, aircraft and electrical manufacturers, and national governments have standards of their own covering the usual refinery products as well as specialty oils peculiar to their needs. The refiner supplying a broad market must, therefore, be equipped to conduct tests according to methods designated by the purchaser.

It is obvious that standard tests require standard apparatus but the full significance of this fact in terms of materials required may not be so apparent. To illustrate, consider a very common test; gasoline distillation. For this one determination it is necessary to maintain a stock of at least six distinct items not including metal-ware or heaters. These articles: sample bottle, graduate, thermometer, distilling flask, receiver bath, and report form are short-lived and must be frequently replaced, moreover, the last four items cannot be employed for any other test. While this example may appear extreme it indicates the necessity of materials control in order that routine tests may not be delayed by lack of equipment. A standardized procedure further insures that even those tests infrequently performed will not be hampered by lack of apparatus.

Materials control not only provides the correct apparatus for all tests but it takes into consideration normal breakage and consumption and provides the necessary replacements. By thus maintaining adequate stocks at all times the delays caused by lack of apparatus are prevented. When stocks are unexpectedly depleted rush orders must be jammed through at additional expense while the testing force is handicapped and must work under extra pressure to provide tests during the shortage. If, as frequently happens, tests are delayed on contract orders, serious mistakes or even loss of business may result. A less costly effect is the disruption of the routine schedule with consequent hindrance of the manufacturing and shipping departments. Naturally the laboratory loses standing with the departments so affected. The laboratory is expected to turn out results, and any failure to do so militates against it.

FREQUENT REPLACEMENTS DESIRABLE

Where the problem has not been studied and a workable plan adopted it is customary to wait until someone reports that the supply of a certain item is exhausted before reordering. That means being out of stock for two or three weeks except for those laboratories located in large centers. In an effort to avoid running out so often, one or even two years' supply of some items may be ordered using the quantity discount as a plausible excuse. Such methods never become crystalized into routine because no one ever gives a thought to replacements until the current stock is gone. Where large orders are placed once or twice a year the size of the last one cannot be remembered and it is too far back to be looked up. Consequently guesswork is the only criterion for quantity requirements and the new order usually is far too large just to be on the safe side. The large stocks thus accumulated make it unduly expensive to conform to changing conditions. Testing methods become obsolete and are replaced just as with processes in the plant. If large inventories are carried there is always the danger that a change of methods will make some of it useless. The writer knows of instances where large cases of obsolete glassware have been taken out of active stock and put in storage. The special items were no longer used and could not be returned for credit.

Difficulties of this nature can be avoided by setting up a workable procedure for materials control. A surprisingly small amount of time and energy is required to determine actual requirements for the items most commonly used. The first step: analyzing purchases for the past year or two is quite laborious but the information thus gathered is invaluable and can be obtained in no other way. This analysis requires going through the requisition files to obtain sufficient figures for calculating consumption. At the same time a list of the currently required items is compiled for use in organizing and classifying storage. The next step calls for a thorough check-up of the stock room. Broken, useless and obsolete articles must be removed for it is practically impossi-

ble to maintain an organized stock room if such material is given adjacent storage. The remaining items, which should include all those listed during analysis of past requisitions plus some additional apparatus seldom used, must then be inventoried and allotted space. For convenience in making withdrawals and placing new stock it is advisable to prepare and post a stock room index.

The inventories are then checked against purchases to determine consumption for the period. In those cases where stocks have lacked proper arrangement it will not be uncommon to discover that certain items have been ordered and reordered when all the time there was an adequate supply in the stock room, probably under some dead stock that had not been touched in years.

Once the consumption is determined it is necessary to decide how often to reorder. Many purchasing agents have learned by actual trial that ordering standard articles for not more than three months in advance permits optimum adjustment to the market. This period has been found to be suitable for most laboratory supplies and makes for convenience in referring to previous orders. As noted earlier in this paper, if materials are ordered for periods of a year or so it is much more difficult to locate previous requisitions and the correlation between size of order and actual requirements cannot be so accurately determined. Also a notable saving in stock room space results from ordering smaller quantities. By adopting the three-month period the maximum amount to reorder is at once established as 25 percent of annual consumption. It must be remembered that these first figures for consumption are preliminary and should be revised periodically to conform to changing conditions. They are, however, sufficiently accurate for stock arrangement and the initial orders. The next factor to be arrived at is the minimum stock to carry before reordering. This is governed by the length of time required to get delivery; that is, replacements should be ordered far enough in advance that stocks on hand will not be exhausted before delivery is made.

After setting up maximum stocks to order and minimum stocks to carry, space in the stock room may be allocated for each item. The actual arrangement will be governed by the facilities available but several important points must be observed. The plan must be both logical and convenient to save time in locating apparatus and sufficient room must be reserved for the maximum amount to be stocked. This last permits placing new purchases directly in the proper place without rehandling. As for logic and convenience, it may be logical to store various sizes of beakers nested together but the resulting inconvenience far outweighs the saving in space.

With the stock room properly arranged it is essential to keep it orderly and well stocked. To do so requires a practical, convenient plan which involves a minimum of time for its operation. The maintenance of adequate supplies should be made as thoroughly routine as possible so that replacements will be received regularly in keeping with demand. The following procedure has been in use for over two years and can be adapted to different conditions. Quarterly requirements were established from analysis of the previous two years orders. The average time required for delivery was determined and on that was based the minimum stock to carry before reordering. As each requisition is written a note is made on the desk calendar for three months hence. When that date turns up the requisition is referred to and a check made of stock on hand. If the minimum stock figure has been reached the same quantity is reordered. If stock on hand is excessive consumption is estimated and a future ordering date selected. On this date reference is made to the original order on which was noted the inventory at three months. Then, if the condition of the stock warrants reordering, the quantity requisitioned is adjusted to requirements.

SPECIAL ITEMS

Special items which are seldom used should be ordered in very small lots. Usually they are expensive and there is always the risk that the need for them will vanish because of changes in products or methods. As many items as possible should be included in one order to minimize clerical effort and to lower shipping costs. With the average shipping time in mind, back orders should be checked to insure prompt delivery. Each shipment should be carefully checked on receipt and then placed in stock. By noting the date of receipt on each requisition a record is made of shipping time for future reference.

The time required to operate this system of materials control is very slight in view of the benefits obtained. In the beginning, of course, the effort involved is substantial but once the routine is established the results far outweigh the cost. The most conspicuous effect is that stocks do not become exhausted nor do they accumulate to excess. Supplies of articles which are not in demand are allowed to shrink to a minimum with the result that dead stock is not likely to amount to more than a few weeks supply at most. The rapid turnover keeps the stock in good condition since most of it will be less than three months old. The smaller storage space required is easier to inventory and keep organized. Reordering is simplified by referring to previous requisitions instead of searching through catalogs for the necessary data. (Duplicates of all requisitions are, of course, filed in the laboratory office).

It may come as a surprise to find that there is an actual cash saving in materials control. The frequent checking of stock brings to light any extraordinary destruction and tends to lower normal breakage. In the case of thermometers and hydrometers, which are both expensive and fragile, the annual saving may amount to hundreds of dollars. The quality of receipts is kept more clearly in mind and money can be saved by dropping inferior grades when new orders are placed.

Materials control is necessary for the smooth operation of any laboratory and is essential to its economy. Oil cannot be tested without apparatus and it is this function which provides an adequate supply. It is always desirable to eliminate lost time in the laboratory and to avert plant complaints of poor service. A method has been described for readily maintaining standard supplies of all laboratory materials. The necessary control is exercised by organizing storage, systematizing purchases, and reducing waste. The advantages which result from small inventories of complete, modern apparatus and an adequate means of checking consumption overshadow the effort and time involved.